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Laboratory Studies and Preliminary Evaluation of Destructive Technologies for the Removal of RDX from the Water Waste Stream of Holston Army Ammunition Plant

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Final report

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Abstract: Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is the primary constituent in the explosive munitions that are produced at Holston Army Ammunition Plant (HSAAP), Kingsport, TN. Part of a modernization effort for the 66-year-old plant includes the goal of zero RDX discharge to the facility industrial wastewater treatment plant. This study examines multiple technologies for removing RDX from the process waste stream at Holston Army Ammunition Plant. The treatment technologies evaluated included granular activated carbon (GAC), anoxic biotreatment, zero-valent iron (ZVI), alkaline hydrolysis, ultra-violet oxidation, and electrochemical decomposition. Evaluation criteria include capital and operating cost, and effectiveness in transforming RDX to nontoxic end products. Based on laboratory assessments using site water, alkaline hydrolysis and electrochemical treatment were selected for pilot scale evaluation. The RDX removal half-lives for the selected technologies were on the order of 0.25 hr with decomposition of RDX from 10,000 µg/L to less than 20 µg/L.

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Executive Summary

Holston Army Ammunition Plant (HSAAP) is a manufacturer of military explosives located in Kingsport, TN. The Tennessee Department of Environmental Compliance (TDEC) is in the process of establishing a total maximum daily load (TMDL) that will regulate the mass of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) that HSAAP may discharge to the Holston River. In August of 2007, a project delivery team was formed including stakeholders from BAE Systems, Joint Munitions Command, and PEO Ammo, along with technology experts from the US Army Armament Research Development and Engineering Center (ARDEC), National Defense Center for Energy and the Environment (NDCEE), Stevens Institute of Technology, and the US Army Engineer Research and Development Center (ERDC) to evaluate possible primary treatment systems to remove RDX from the water waste stream at HSAAP.

Several technologies exist and have been demonstrated for the treatment of RDX-laden waters. Most of these technologies have been developed as treatments for contaminated groundwater. The objective of this work is to evaluate potential abiotic pretreatment systems for the destruction of RDX in HSAAP waste streams. Previous efforts have evaluated the cost of using a non-destructive technology such as granular activated carbon (GAC) (US Army Center for Health Promotion and Preventative Medicine (USACHPPM) 2005). Sorption processes are generally undesirable because they generate a contaminated and possibly explosive residual waste stream that requires additional handling. This report surveys several options for destructive removal of RDX from an industrial liquid waste stream and provides data for the performance of selected technologies in treating wastewater obtained from HSAAP. The focus is on developing an innovative, effective, low cost treatment method based on contaminant destruction. The work reported herein details the laboratory evaluation of alkaline hydrolysis, direct electrochemical reduction, and ultraviolet (UV) oxidation.

At this stage of development, the main points of comparison are 1) treatment effectiveness and efficiency, and 2) operating cost of the proposed systems. Total operating costs include factors such as maintenance that are not addressed during a bench scale evaluation, but a

preliminary analysis may be made based on the major expected input cost. For alkaline hydrolysis, this would be the chemical cost of pH adjustment. For UV oxidation and electrochemical reduction, this would be the energy cost. Alkaline hydrolysis exhibited the highest potential operating costs, but merited further study given the potential for much lower capital costs. Alkaline hydrolysis has the advantage of being the simplest system available, as adding base requires no specialized equipment. The UV lamps required for ultraviolet oxidation have high energy requirements and direct electrochemical reduction requires much lower energy input. Two direct electrochemical configurations were evaluated: 1) a sequencing batch reactor tank with rotating electrode impellers, and 2) a continuous flow reactor packed with electrode plates.

In order to determine the best option for a full-scale treatment plant, pilot scale reactors should be built which allow for a more reliable evaluation of technology effectiveness, operating cost, and capital cost. The resulting study would be a pilot evaluation of the two direct electrochemical reduction configurations and one alkaline hydrolysis configuration. Information developed during the pilot will lead to a complete cost analysis of alternative primary treatment systems to remove RDX from a process waste stream.

Preface

This report presents the results of a study funded by MIPR number HI7G3046HIF6 through the U.S. Army Armament Research, Development and Engineering Center (ARDEC), Picatinny, NJ, and under the direction of Greg O'Connor.

This study was performed by Dr. Steven Larson, Deborah Felt, Dr. David Gent and Jared Johnson, Environmental Engineering Branch (EP-E), Environmental Processes and Engineering Division (EPED), Environmental Laboratory (EL), U.S. Army Engineer Research and Development Center (ERDC) and Mr. Gregory O'Connor, ARDEC. The authors were assisted by Michelle Thompson and Catherine Nestler (Applied Research Associates, Inc.) and Deborah Ragan (SpecPro, Inc.). Danny Averett and Damarys Acevedo provided technical review.

This study was conducted under the direct supervision of W. Andy Martin, Branch Chief, EP-E, and under the general supervision of Dr. Richard E. Price, Division Chief, EPED, and Dr. Elizabeth C. Fleming, Director, EL.

At the time of this study COL Gary E. Johnston was Commander and Executive Director of ERDC. Dr. James R. Houston was ERDC Director.

Unit Conversion Factors

Multiply	By	To Obtain
gallons (U.S. liquid)	3.785412 E-03	cubic meters
inches	0.0254	meters
pounds (mass)	0.45359237	kilograms

Acronyms

EL	Environmental Laboratory
ERDC	Engineer Research and Development Center
gdp	gallons per day
HSAAP	Holston Army Ammunition Plant
RDX	Royal Demolition Explosive
USACHPPM	U.S. Army Center for Health Promotion and Preventive Medicine
USEPA	U.S. Environmental Protection Agency

1 Introduction

Holston Army Ammunition Plant (HSAAP) is a manufacturer of military explosives located in Kingsport, TN. The facility was constructed in 1942, and has remained in continuous operation since then. It is currently operated under contract from the Department of Defense (DoD) by BAE Systems, Inc.

The Tennessee Department of Environment and Conservation (TDEC) is in the process of establishing a total maximum daily load (TMDL) that will regulate the mass of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) that HSAAP may discharge to the Holston River. Previous studies have established that the existing wastewater treatment facility removes ~50% of the RDX mass from the HSAAP waste stream. This is insufficient to meet the new TMDL, so a pretreatment system will be required to remove additional RDX mass from the water waste streams at HSAAP.

Several technologies have been demonstrated or used full scale for the treatment of RDX-laden waters. Most of these technologies have been developed to treat contaminated groundwater. The objective of this work is to evaluate three potential pretreatment systems, alkaline hydrolysis, direct electrochemical reduction, and ultraviolet oxidation, for the destruction of RDX in HSAAP waste streams. Previous efforts have evaluated the cost of using a non-destructive technology such as granular activated carbon (GAC) (U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM 2005). Sorption processes are generally undesirable because they generate a contaminated and possibly explosive residual that requires further handling. This report surveys several options for destructive removal of RDX from an industrial liquid waste stream and provides data for the performance of selected technologies in treating wastewater obtained from HSAAP. The focus is on developing an innovative, effective, low-cost destructive treatment method.

2 Literature Review

Hexahydro-1,3,5-trinitro-1,3,5-triazine, also known as cyclotrimethylene-trinitramine, cyclonite, or RDX (Figure 1) is a powerful military explosive. The basic properties of RDX are given in Table 1. RDX was first synthesized and patented by Henning (1899). A complete synthesis reaction was published by Hale (1925), and an alternative synthesis was discovered by Bachmann and Sheehan in 1941 and published later (1949). The United States Environmental Protection Agency (USEPA) has determined RDX to be a possible carcinogen and set the lifetime drinking water health advisory at 2 µg/L (USEPA 2004).

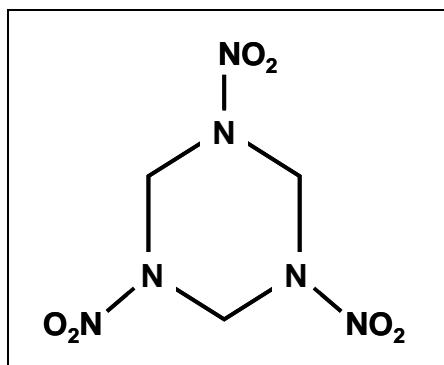


Figure 1: Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX).

Table 1. Selected properties of RDX.

CAS Number	121-82-4
Empirical formula	C ₃ H ₆ N ₆ O ₆
Molecular weight	222.26 g/mol
Density	1.82 g/cm ³
Melting point	204.1 °C
	29 mg/L (10 °C)
	42 mg/L (20 °C)
Aqueous solubility	60 mg/L (25 °C)

Significant research has been accomplished to determine the environmental fate and transport of RDX (Brannon and Pennington 2002). RDX is stable in soil slurries under moderate pH and oxidizing to moderately reducing conditions, but is unstable under highly reducing (-150 mV) conditions (Price et al. 2001). RDX degradation at low oxidation-reduction

potentials occurs in both biotic and abiotic systems. While RDX is stable at low and neutral pHs, it is unstable at high pH. Significant groundwater contamination is currently being treated at the former Nebraska Ordnance Plant (Wani et al. 2007) and Camp Edwards, MA (Clausen et al. 2003). In each case, RDX-laden water streams are currently being treated ex situ by adsorption onto granular activated carbon.

Treatability studies have determined that RDX is removed from aqueous solution by several grades of granular activated carbon (GAC) (Fleming et al. 1996, Bricka and Fleming 1995). This is a nondestructive technology; the RDX remains adsorbed on the carbon surface. Once the sorptive capacity of the carbon has been reached, it must be disposed of properly or regenerated by removing and treating the sorbed RDX. One constraint on used GAC is that the loading of explosives must not exceed 10% w/w or the carbon is considered explosive under Department of Transportation Guidelines. Reports indicate that explosive reactions may occur at loadings of ~10% (Oak Ridge National Laboratory (ORNL) 1988) and 8% (Andern et al. 1975). The Army Environmental Command, along with EPA Region 10 and the Oregon Department of Environmental Quality, has set the characteristic hazardous waste status of explosives laden soils at 12% (Noyes 1996). Thermal regeneration of potentially explosive carbon is not recommended, though acetone (Fleming et al. 1996) and ethanol (Morley et al. 2005) have been studied as facilitators of RDX desorption from GAC. Solvent regeneration in this manner yields an RDX-laden solvent waste stream that must be treated, as well.

Alkaline hydrolysis of RDX has been reported since 1951 (Epstein and Winkler 1951). Balakrishnan et al. (2003) proposed the mechanism of alkaline destruction of RDX detailed in Figure 2. Kinetic rates for this reaction have been reported in aqueous solutions (Heilmann et al. 1996, Hwang et al. 2006) and soil slurries (Brooks et al. 2003). The end products of alkaline hydrolysis at pH above 12 are primarily formate and nitrate (Davis et al. 2007). Alkaline hydrolysis is a relatively rapid and easy treatment for contaminated water and soil. It has been effectively demonstrated on active training ranges through the application of hydrated lime (Larson et al. 2008).

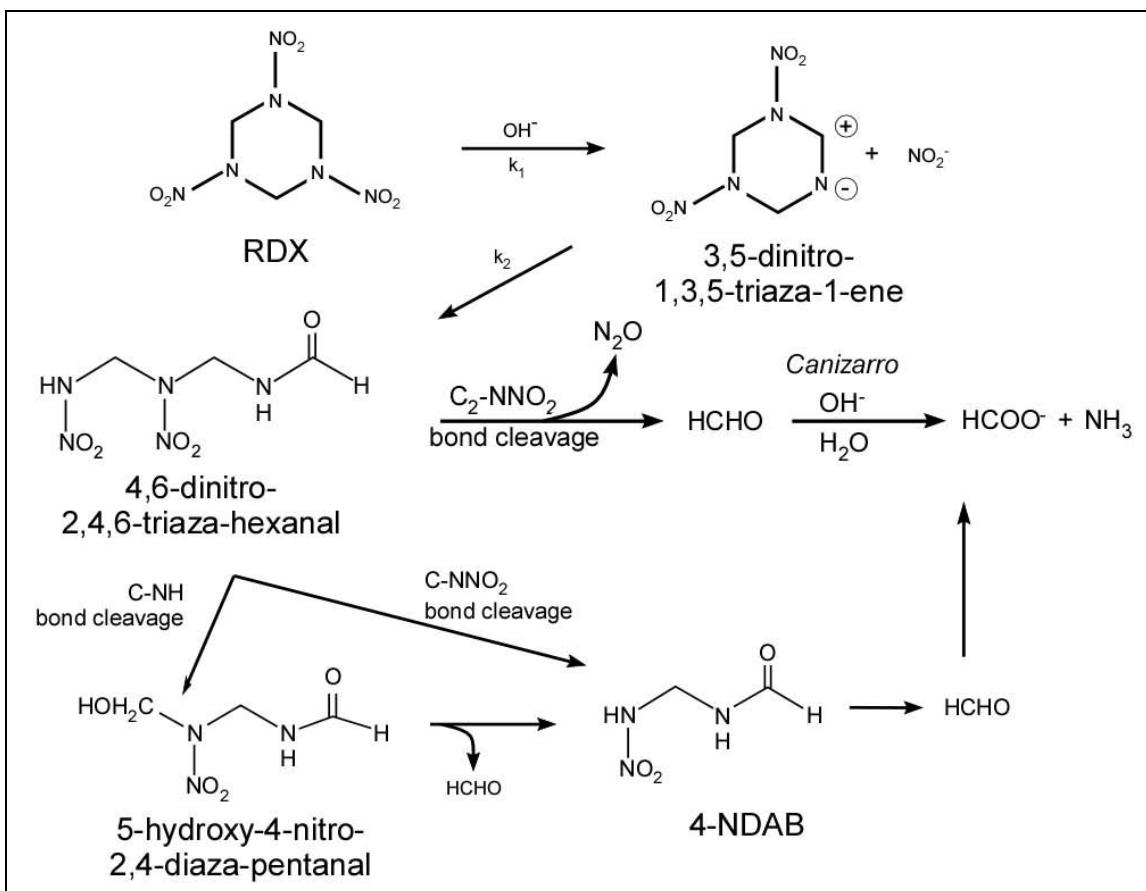


Figure 2. Mechanism of RDX destruction by alkaline hydrolysis proposed by Balakrishnan et al. (2003).

Electrochemical reduction of RDX has been reported by several groups (Pehkonen et al. 1999, Bonin et al. 2004, Gilbert and Sale 2005, Wani et al. 2005). A proposed mechanism from Bonin et al. (2004) is detailed in Figure 3. Electrochemical reduction has been investigated as a wastewater treatment technology (Doppalapudi et al. 2001) and for in situ treatment of contaminated groundwater (Wani et al. 2005, Gilbert and Sale 2005). The relevant wastewater applications made use of vitreous carbon electrodes in separate compartment electrochemical reactors. In both cases, the final products of RDX transformation were observed to be small organic compounds (formate, formaldehyde, nitrate) without buildup of the nitroso breakdown products. Direct electrochemical destruction has not been demonstrated at the field scale.

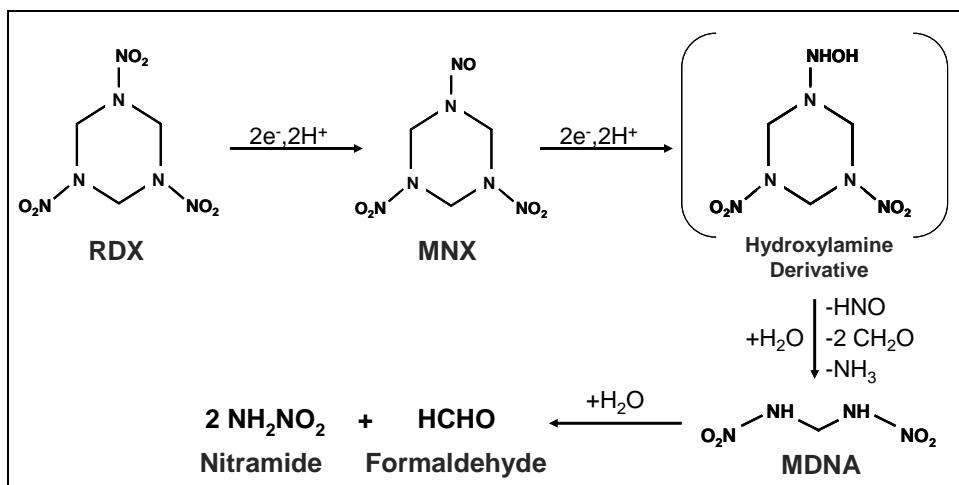


Figure 3. Mechanism for the direct electrochemical reduction of RDX in aqueous solution proposed by Bonin et al. (2004).

RDX has proven susceptible to anaerobic biodegradation under a range of cultures and nutrient additions (Freedman and Sutherland 1998, Wani and Davis 2006, Beller 2002, Binks et al. 1995). In situ biodegradation has been stimulated with the addition of both electron donors (Beller 2002) and readily available carbon sources (Wani and Davis 2006). Freedman and Sutherland (1998), with others, have reported that the presence of nitrates inhibits the transformation of RDX. This study specifically used a biological culture obtained from the anoxic filter at the HSAAP industrial wastewater treatment plant. It determined that the microbes present could reduce RDX in the HSAAP waste stream, though this would not occur until nitrates present in the system have been completely reduced. Bioremediation has been successfully demonstrated at the field scale as an in situ groundwater treatment (Wani et al. 2007) and as a water treatment system in upflow fluidized bed reactors (Atikovic et al. 2008).

Iron and ferrous minerals have been demonstrated to degrade RDX in biologically active systems (Shrout et al. 2005, Oh et al. 2001, Wildman and Alvarez 2001), as stand-alone mineral surfaces (Park et al. 2004, Hundal et al. 1997, Wanaratna et al. 2006), as nanoparticles (Naja et al. 2008), and as ions in solution (Kim and Strathmann 2007). Investigations into the use of zero-valent iron have developed applications as permeable reactive barriers (Hundal et al. 1997), and as industrial wastewater treatment units (Oh et al. 2006).

Other unique technologies have been investigated for the destruction of RDX in environmental matrices. Various oxidative processes have been

investigated for the degradation of RDX in water and soils (Bose et al. 1998a, 1998 b; Adam et al. 2006, Fleming et al. 1997). These technologies make use of ultraviolet light either alone or in conjunction with chemical oxidants such as ozone or hydrogen peroxide. Advanced oxidation processes have been compared for treatment of RDX-laden water ex situ (Fleming et al. 1997). Additional treatment technologies reported in the literature include nickel catalysts (Fuller et al. 2007), permanganate (Adam et al. 2004), plasma arc (Elmore and Lee 1999), hydrogen sulfide (Kemper et al. 2008), mulch barriers (Ahmad et al. 2007), constructed wetlands (Low et al. 2007), and dithionite reduction (Boparai et al. 2008).

This report presents the results of bench scale investigations of the potential for alkaline, electrochemical, and ultraviolet light technologies to provide low cost, innovative solutions for the primary treatment of RDX in the water waste stream of HSAAP.

3 Alkaline Batch Studies

Materials and methods

Wastewater laden with RDX was collected from the HSAAP sewer system at manhole P-6 for use in all laboratory batch studies of RDX degradation technologies. Six 55-gallon drums of water were filled and taken to the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS. Drum analyses in Table 2. Four of the drums contained from 9.13 to 10.03 mg/L of RDX with little variation between them. Two of the drums contained much higher concentrations (16.84 and 27.28 mg/L, respectively) even though the drums were filled within minutes of one another from the same source. The most likely explanation for the variation is that particles of RDX were either entrained in the wastewater stream or dislodged from the floor of the discharge system and entered drums 3 and 6 during sampling. Each of the drums exhibited consistently neutral pH and $\sim 300 \mu\text{S}/\text{cm}$ conductivity. The total alkalinity of the collected wastewater was determined by acid titration to be 18 mg CO₃/L. The HSAAP water was analyzed by inductively coupled plasma spectroscopy (ICP) following USEPA method 200.7 (USEPA 2001) to determine the calcium and magnesium concentrations and hardness. The calcium and magnesium concentrations were 32.9 mg/L and 8.4 mg/L. The calcium, magnesium, and total hardness from the sample was calculated to be 82.2, 34.6, and 116.8 mg/L as CaCO₃.

Table 2. Selected properties of collected wastewater.

Drum #	pH	Conductivity ($\mu\text{S}/\text{cm}$)	RDX (mg/L)
1	7.30	304	9.77
2	7.33	303	9.13
3	7.32	308	16.84
4	7.35	308	10.03
5	7.36	310	9.43
6	7.26	304	27.28

The triplicate batch reaction system used for initial evaluation of destructive technologies is detailed in Figure 4. Batch alkaline hydrolysis experiments were performed in triplicate using 500-mL aspirator bottles (Corning No.: 1220) as batch reactors. The aspirator bottle outlet was connected with clear, thin-walled Tygon® tubing through a two-way zero volume normally closed solenoid valve (Cole-Parmer®, 16 LPM, 12 VDC, C-01367-70) to 3.175 mm ID Tygon® tubing connected to an Eldex Universal Fraction Collector (UFC) base (#1243) unit with a UP-50 preparation rack containing 20-mL scintillation vials. A custom panel mounted timer/controller was assembled to operate three solenoid valves and to advance the fraction collectors to the next position by means of eight programmable digital timers (Atonics LE3S) and three 0.5-Amp SPST Reed Relays (Radio Shack Model: 275-233, 12Vdc). Each sample collection cycle consisted of a global time, outlet purge, tray advance, sample collection, and another tray advance.

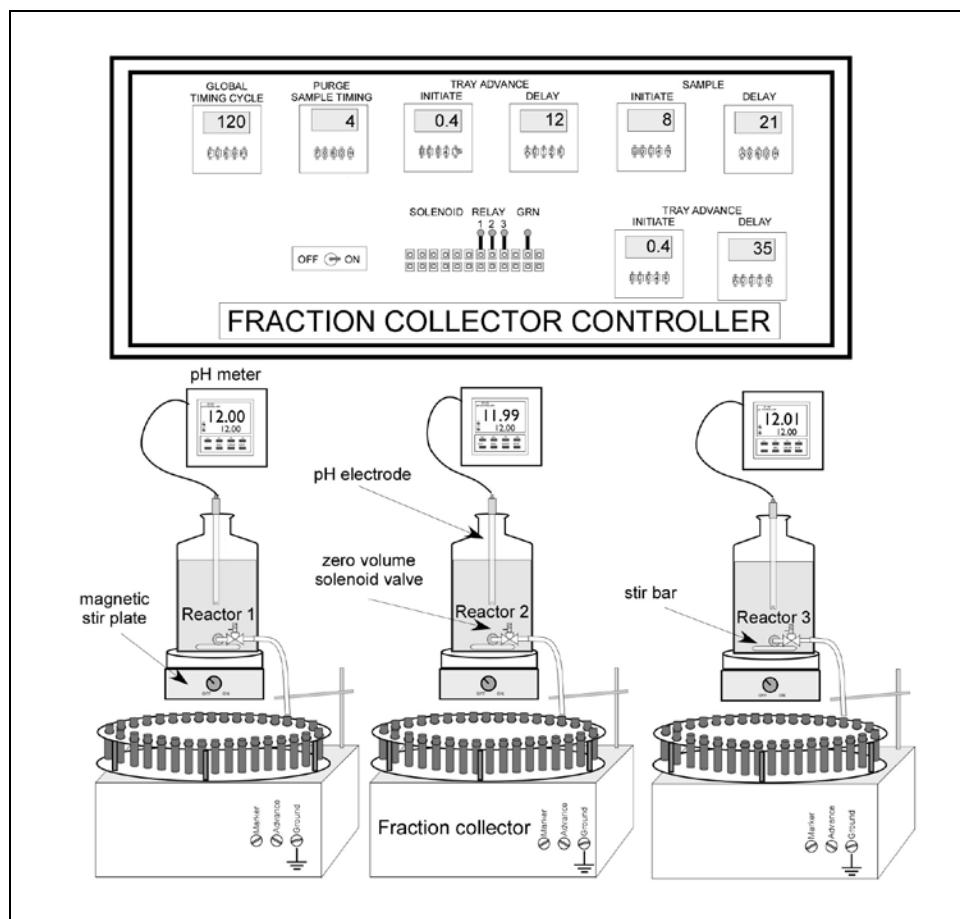


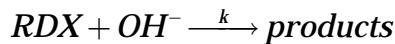
Figure 4. Timer/controller system used for triplicate batch experiments.

Three pH meter/controllers (SK-631/632 Pathfinder, Carlsbad, CA) were equipped with Sensorex S200CD double junction pH electrodes to monitor pH during the experiments. The pH electrodes were calibrated with pH buffers 7.0, 10.0, 12.0, and 12.45 depending on the target pH required. The pH electrode exposure time to these hydroxide concentrations was limited to 5 minutes at sample collection time; electrodes were then stored in a pH 7.0 buffer solution between measurements. All liquid samples from the reactors were spiked with an appropriate volume (50 to 100 μ L) of 2-M hydrochloric acid to quench the alkaline hydrolysis reaction by lowering the sample pH below 3.0. At pH values of 13 and 13.3, pH electrodes proved inadequate for monitoring the experimental conditions. For these tests, the total sample weight was recorded along with the acid quench volume and final pH. Initial pH was then calculated using a titration equation.

Each reactor was loaded with 500 g of process wastewater at the start of the experiment. The initial pH was adjusted by adding 0.25-5 g of 50% (w/w) NaOH depending on the target reaction pH. Sampling removed approximately 15 mL per sample event from the reaction volume. The reaction pH was monitored throughout the experiment, and additional NaOH was added as necessary to maintain the target pH. Each experiment was carried out at 22° C.

Alkaline batch kinetics results and discussion

Chemical kinetic reaction rates were determined by the isolation method, since the concentration of hydroxide was 22 – 7000 times higher than the RDX concentration. The unbalanced reaction is



Equation 1: The unbalanced chemical reaction of RDX and hydroxide ion.

The rate law for this chemical reaction is

$$r = k[RDX]^a[OH^-]^b$$

Equation 2: Rate law for the reaction of RDX and hydroxide ion.

where k is the reaction kinetic rate constant and the exponents are unknown reaction orders. The hydroxide concentration remained

essentially unchanged throughout each experiment allowing the hydroxide component of the rate law to be included in the reaction constant. The observed reactions support using a first order ($a = 1$) model such that

$$r = k_{app} [RDX]$$

Equation 3: Rate law supporting a first order model for the reaction of RDX and hydroxide.

where k_{app} is the first order reaction rate coefficient (T^{-1}) for RDX with respect to time. A first order decay kinetic constant k_{app} was determined for RDX concentrations versus time for each hydroxide concentration tested by fitting the observed data to

$$C = C_0 e^{-k_{app}t}$$

Equation 4: Calculation for the first order decay kinetic constant for RDX versus time for each hydroxide concentration.

where C is the instantaneous concentration of RDX, C_0 is the initial concentration, and t is the reaction time. Results of these experiments were analyzed statistically using nonlinear regression modeling where time was the independent variable (x-coordinate) and the repeated replicates of [RDX] were the dependant variable (y-coordinates). The analytical data from the batch titration results were modeled with a two-parameter nonlinear exponential decay equation to determine apparent first order reaction rate coefficients with respect to RDX concentration (Equation 4). The statistical software SigmaPlot® uses the Marquardt-Levenberg algorithm to determine the parameters that minimize the sum of squares of differences between the RDX concentration values predicted by the equation model and the observed values.

The samples collected from the triplicate batch titration experiments at four concentrations of hydroxide ions (pH 12, 12.5, 13 and 13.3) were analyzed by high pressure liquid chromatography (HPLC) following USEPA Method SW-846 Method 8330 (USEPA 1994) to determine RDX concentrations at specific time intervals. Alkaline hydrolysis reaction rate coefficients are summarized in Table 3 by pH with RDX concentration, rate coefficient, and calculated half-life ($\ln(2)/k$). The batch hydrolysis results along with corresponding predicted fit are plotted by RDX concentration versus time in Figure 5.

Table 3. First order reaction coefficients for alkaline destruction of RDX.

pH	Hydroxide Concentration (mM)	Initial RDX Concentration (mg/L)	1 st Order Kinetic Rate Constant k (hr ⁻¹)	Standard Error of k (hr ⁻¹)	Half Life (hr)
12.0	10	9.63	0.16	0.01	4.4
12.5	32	8.91	0.50	0.06	1.4
13.0	100	6.85	1.61	0.03	0.4
13.3	200	6.09	3.14	0.05	0.2

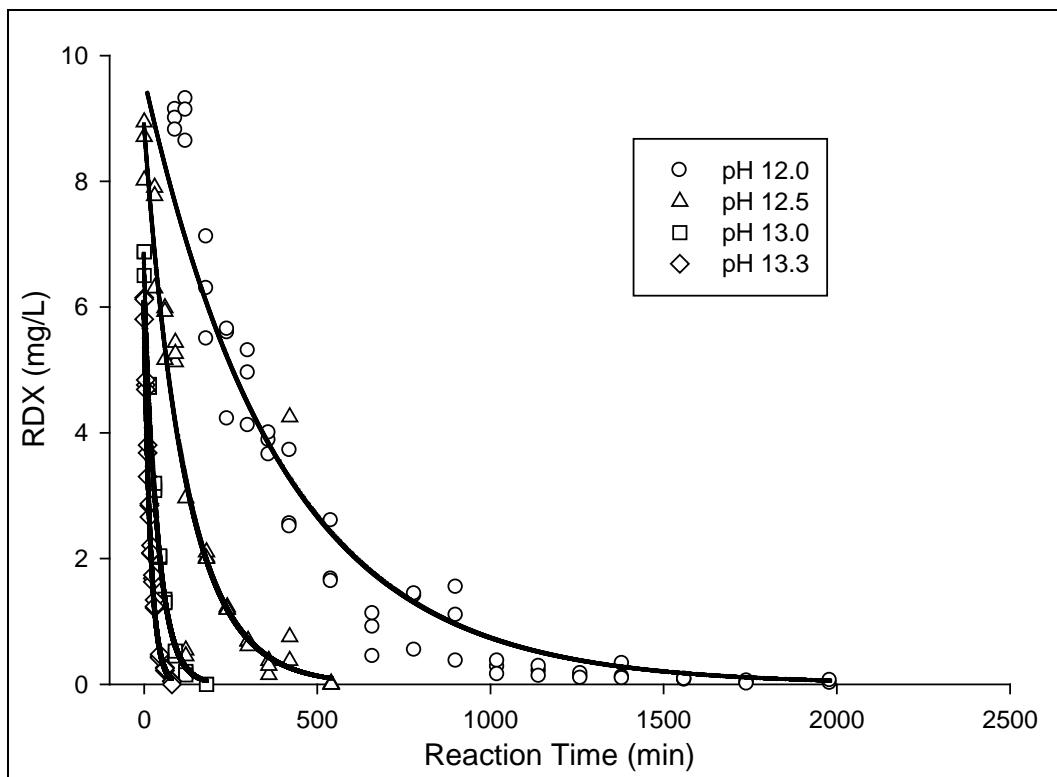


Figure 5. RDX degradation with time at varying pH.

The half life of RDX decay, and hence the total required treatment time in batch reactions, was inversely related to the hydroxide concentration. The relationship of hydroxide concentration to the apparent first order kinetic rate is detailed in Figure 6. Over the range of concentrations studied, the rate constant increases proportionally with hydroxide concentration according to:

$$k = 0.0156[OH^-]$$

Equation 5: Calculation of the rate constant for the reaction of RDX with hydroxide.

where k is given in hr^{-1} . This indicates that the previously unknown reaction order on $[\text{OH}^-]$ (b in Equation 2) may be described as 1, and the total rate law for decay of RDX in HSAAP industrial sewer water may be described as

$$\frac{dC}{dt} = 0.0156[\text{RDX}][\text{OH}^-]$$

Equation 6: The total rate law for the decay of RDX in industrial wastewater.

where C is the instantaneous RDX concentration, t is the reaction time, and 0.0156 is the second order rate constant in $(\text{hr}\cdot\text{mM})^{-1}$.

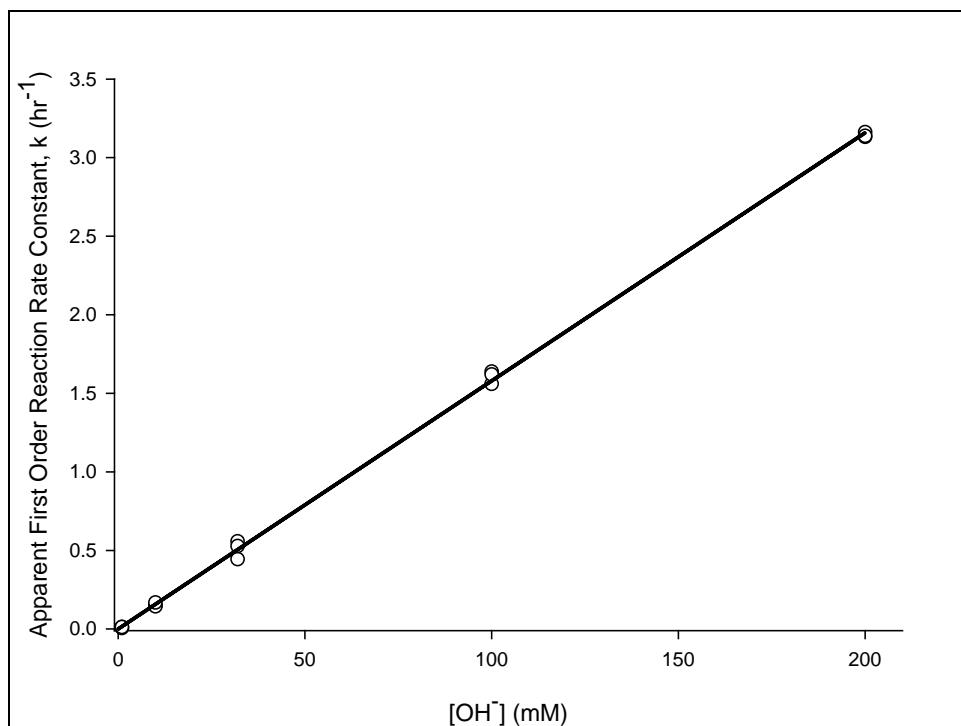


Figure 6. Relationship of hydroxide concentration to the apparent first order decay rate of RDX in HSAAP industrial wastewater.

The major operating cost component of an alkaline hydrolysis treatment system will be the chemical addition required to raise and lower pH. The freight-on-board (shipping point) cost of sodium hydroxide according to a quote obtained 23 September 2007 was \$ 0.22 per pound. The cost of sulfuric acid for neutralization was \$ 0.15 per pound. If treatment is accomplished at pH 13, these estimates result in a total chemical cost of \$0.02 per gallon treated.

At the end of each alkaline experiment the stir plates were turned off and the water in each reactor was allowed to settle. Visual inspection noted traces of a light white precipitate in the bottom of each reactor. Since the HSAAP water contains both calcium and magnesium, some precipitation was expected. The precipitate masses were measured by removing the water remaining from each batch reactor experiment. The water was poured through a filter, dried, and weighed to determine the precipitated solids.

The precipitate mass for each replicate experiment is shown in Table 4 along with its mean and standard deviation by pH. The pH 13 and 13.3 replicates contained the highest precipitate masses. At pH 13 the average solids present were 51.9 ± 11.8 mg. The pH 13 highest replicate (61.9 mg) was used to calculate the mass of precipitate that may be produced by alkaline hydrolysis at the design flows. The estimate shows that 10.3 lb/d of CaCO_3 will be produced at a flow of 10,000 gallons per day (gpd) and 41.2 lb/d of CaCO_3 produced at 40,000 gpd. The majority of the light precipitate mass would be expected to flow out of the reactor with the neutralized effluent into the existing industrial wastewater treatment plant.

Table 4. Mass of precipitate produced for each pH value evaluated by replicate.

Description	pH 12			pH 12.5			pH 13			pH 13.3		
	R1	R2	R3	R1	R2	R3	R1	R2	R3	R1	R2	R3
Weigh Boat Tare (g)	5.87	5.77	5.95	5.92	6.04	5.65	5.70	5.58	5.71	6.08	5.92	6.03
Weigh Boat +Dry Filter (g)	6.37	6.28	6.43	6.42	6.52	6.14	6.20	6.06	6.20	6.46	6.35	6.52
Weigh Boat + Dry Filter + Precipitate (g)	6.39	6.30	6.44	6.45	6.55	6.18	6.26	6.10	6.26	6.42	6.41	6.58
Solids Present (mg)	22.0	21.0	14.6	28.9	22.6	32.5	61.9	38.9	54.9	n/a	57.6	61.6
Mean & Stdev.	19.2 ± 4.0			28.0 ± 5.0			51.9 ± 11.8			59.6 ± 2.8		

Comparison of batch alkaline hydrolysis with published results

Comparison of the experimental coefficients from literature is problematic because of differences in methodologies and the hydroxide concentrations (Table 5). The two previous studies under similar conditions are Hwang et al. (2006) and Gent (2007). The differences among the rate coefficients may be explained by dissimilar dissolved ionic species in the water matrix and experimental procedure used. Given these caveats, the observed reaction rates noted in this study remained higher than those observed in other published studies.

Table 5: Comparison of first-order RDX coefficients from published studies.

Matrix and pH	Results	Gent (2007)	Hwang et al. (2006)
	HSAAP	DI*	DI
	$k_{obs} \times 10^3$ (hr ⁻¹)	$k_{obs} \times 10^3$ (hr ⁻¹)	$k_{obs} \times 10^3$ (hr ⁻¹)
11.5		67.9	102
12.0	156	124.7	138
12.2			474
12.5	504	309.3	
12.6			1338
13.0	1610		
13.3	3140		

HSAAP= Holston water from manhole P-6 in the production area

DI = deionized water

DI* = deionized water with calcium chloride (300 uS/cm conductivity)

4 Electrochemical Batch Studies

Materials and methods

Direct electrochemical reduction of RDX was investigated in mixed compartment electrochemical cells using HSAAP industrial wastewater as the sole electrolyte. Electrodes were constructed of an expanded titanium mesh substrate with a mixed precious metal oxide coating (Corrpro Companies, Medina, OH). This material has 2.46 m² of total surface area per square meter of electrode material. It was purchased in 16-cm by 122-cm sheets and cut to size in the laboratory. Electrical connections were made by physically crimping stranded copper wire to the electrode material and waterproofing the connection with epoxy resin putty.

The batch experimental setup, shown in Figure 7, uses the same automatic sampling system detailed for the alkaline hydrolysis batch experiments. Batch experiments for each condition were carried out with 500 g of RDX-laden water in 600-mL polypropylene beakers. Electrodes were held in the beakers at a submerged depth of 8.9 cm with stir bars providing mixing at 300 rpm. Power was supplied to the electrodes with 500 mA/20 V direct current power supplies (Agilent Technologies, Santa Clara, CA). Experiments were run concurrently in triplicate for each condition. Constructed outlets at the bottom of each beaker were connected with clear thin-walled Tygon® tubing through a two-way zero volume normally closed solenoid valve (Cole-Parmer®, 16 LPM, 12 VDC, C-01367-70) to an Eldex Universal Fraction Collector (UFC) base (#1243) unit with a UP-50 preparation rack containing 20 mL scintillation vials. A custom panel mounted timer/controller was assembled to operate three solenoid valves and to advance the fraction collectors to the next position by means of eight programmable digital timers (Atonics LE3S) and three 0.5-Amp SPST Reed Relays (Radio Shack Model: 275-233, 12Vdc). Each sample collection cycle consisted of a global time, outlet purge, tray advance, sample collection, and another tray advance.

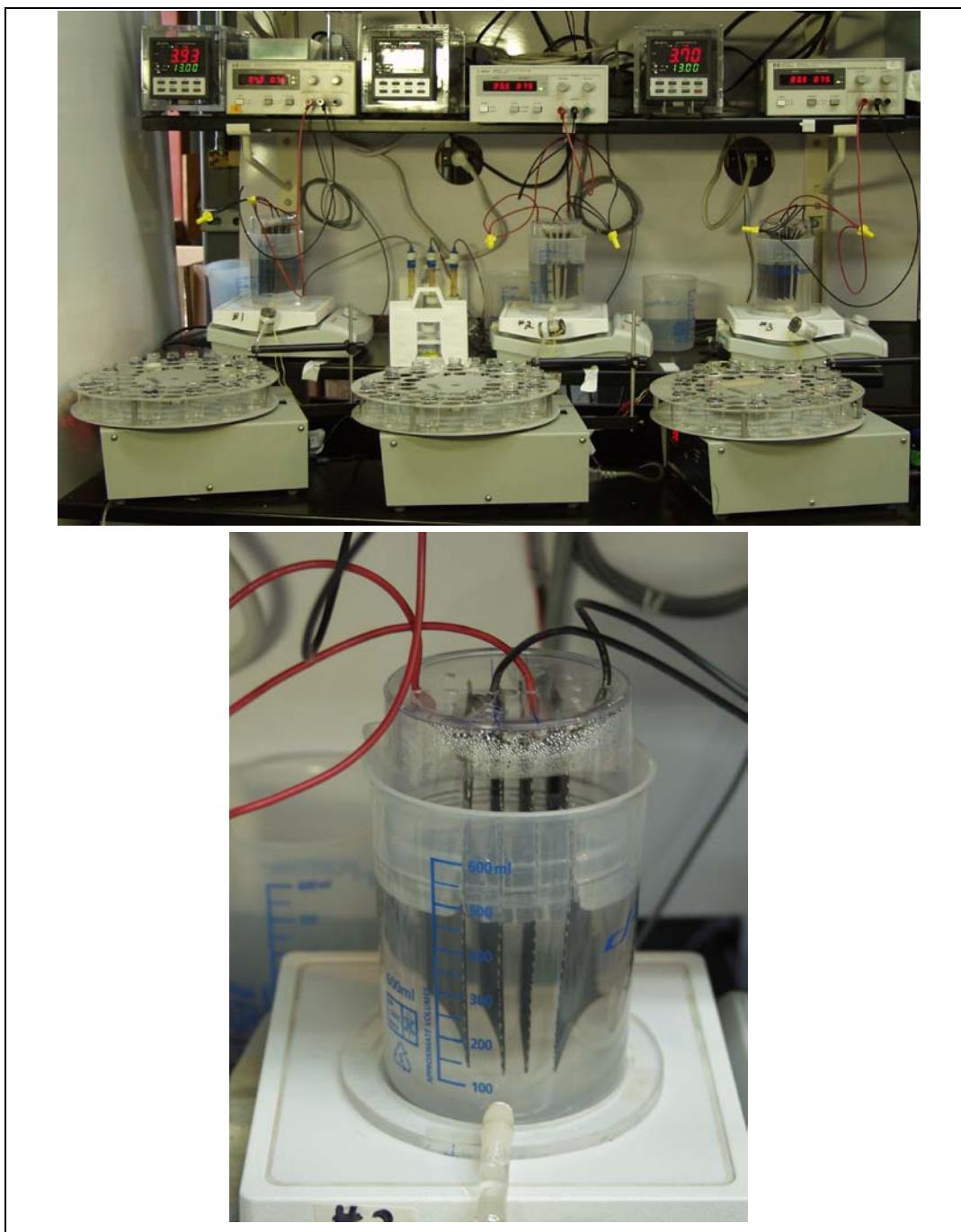


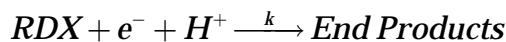
Figure 7. Batch reaction system used to perform electrochemical experiments in triplicate.

Samples of 10-15 mL were removed during experiments at intervals of 5-240 minutes for explosives analysis. At lower current densities, the total reaction time was 24 hr. Reaction times of 6 hr were used at higher current densities. Samples were analyzed for RDX and its associated breakdown products, hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-nitro-1,3,5-triazine (DNX), and

hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX), using HPLC following a modified SWA-846 method 8330 on a Dionex Acclaim EC (cyano) column, utilizing a 1:1 v/v methanol-water mobile phase at 1 mL/min. Absorbance was monitored at 254 nm on an electrode-diode array spectrophotometric detector. Analytes were identified by comparison to retention times of known standards and were quantified using a seven-point standard curve that was linear from 0.05 to 10 mg/L. The analytical data from the batch titration results were modeled with a two-parameter nonlinear exponential decay equation to determine apparent first order reaction rate coefficients with respect to RDX concentration. A statistical software package, SigmaPlot®, used the Marquardt-Levenberg algorithm to determine the parameters that minimize the sum of squares of differences between the RDX concentration values predicted by the equation model and the observed values.

Electrochemical results and discussion

The unbalanced reaction for the electrochemical destruction of RDX is



Equation 7. Unbalanced reaction for electrochemical destruction of RDX

where the end products have been determined as formate, formaldehyde, and nitrate (Gent 2007). This reaction is irreversible, so an appropriate rate law may be hypothesized as

$$\frac{dC}{dt} = k[RDX]^a[e^-]^b[H^+]^c$$

Equation 8. Hypothetical rate law of RDX destruction

where C is the instantaneous concentration of RDX, t is the reaction time, k is the reaction rate constant, a , b and c are reaction order constants, and the individual reactant concentrations all contribute to the reaction rate. Assuming that the electrode efficiencies remain constant through the experiments, this rate law can be reduced to a single order equation:

$$\frac{dC}{dt} = k[RDX]^a$$

Equation 9. Rate law reduced to a single order equation.

Batch experiments exhibited reaction kinetics that fit well with a first order ($a = 1$) rate law, so that the reaction was effectively modeled by

$$C = C_0 e^{-kt}$$

Equation 10. First-order rate law to model electrochemical destruction of RDX.

where C is the instantaneous concentration of RDX, C_0 is the initial concentration of RDX, k is the reaction rate constant, and t is the reaction time.

Electrochemical batch experiments were carried out varying both electrode surface area and current density. Summary results for RDX disappearance at varying electrode surface areas are detailed in Figure 8. The first order reaction rates are shown with respect to electrode surface areas in Figure 9. Across the range of surface areas studied, the reaction rate increased linearly with electrode surface area.

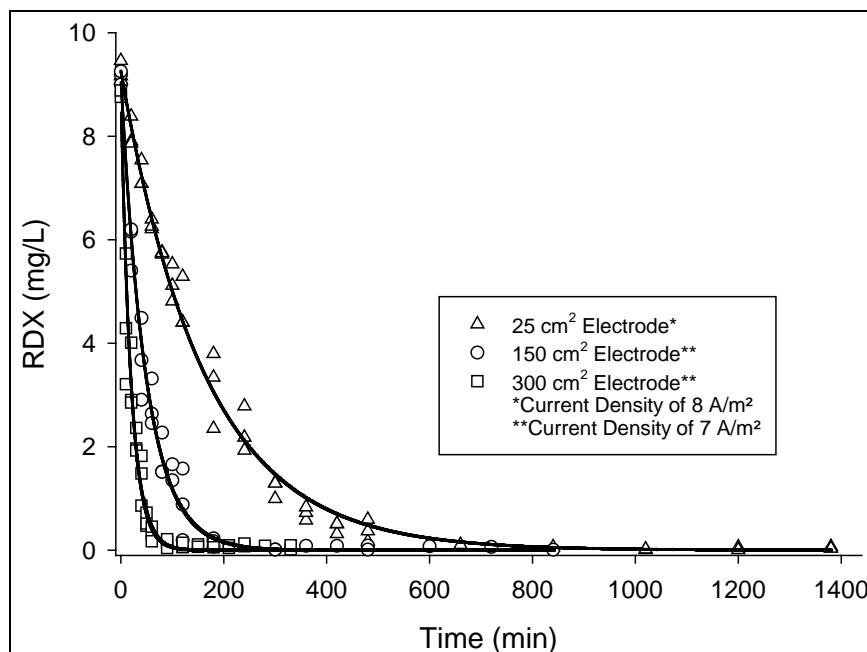


Figure 8. Disappearance of RDX over time in 500-mL electrochemical batch reactors at current densities between 7 and 8 A/m².

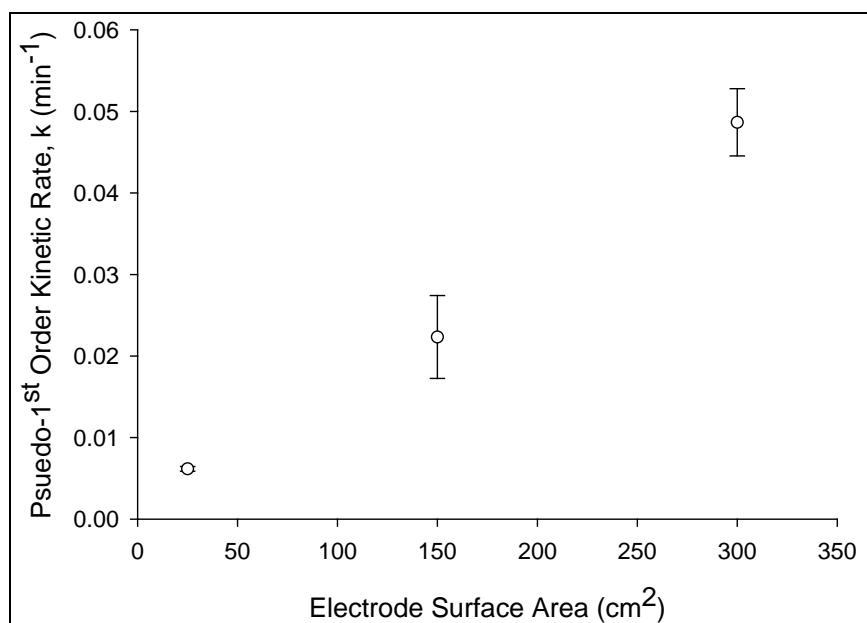


Figure 9: First order reaction rates with varying electrode surface area in electrochemical batch reactors with current densities of 7-8 A/m².

First order reaction rates for RDX degradation in electrochemical batch experiments of varying current densities on 350 cm² of cathode surface area are detailed in Figure 10. Above a minimum current density of 2 A/m², the reaction rate increases with current density. Above 4 A/m², the reaction rate begins to show diminishing returns with increased current density. The point of diminishing returns with increased current density indicates the point at which mass transfer from the bulk fluid to the electrode surface becomes the rate-limiting step in the reaction. The observed rates correspond to the required treatment time in an RDX waste stream as detailed in Table 6. Since process wastewaters may contain saturation levels of RDX, the total treatment time is estimated for 50 mg/L wastewater.

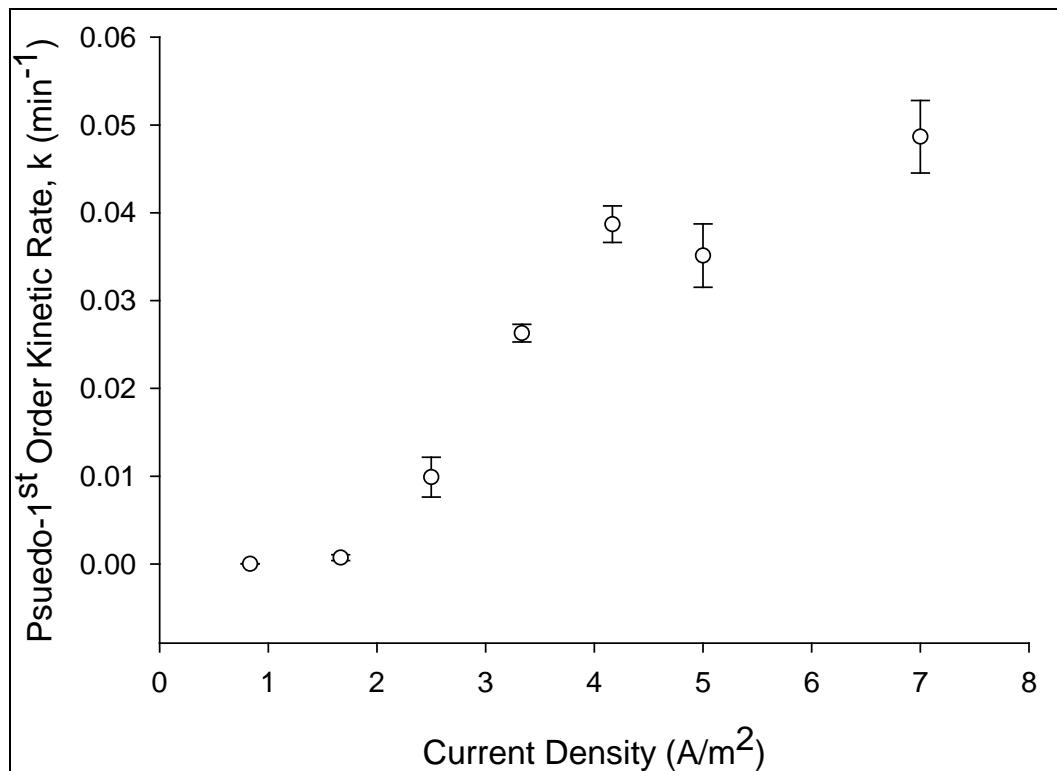


Figure 10. Apparent first order kinetic rate parameter of RDX disappearance in electrochemical batch reactors with varying current density and 350 cm² of cathode surface area (95% confidence intervals).

Table 6. Observed electrochemical half lives and estimated treatment times for saturated RDX in water (95% confidence intervals).

Current (mA)	C.D. (A/m ²)	k (min ⁻¹)	Half Life (min)	Treatment Time (50 mg/L to 2 µg/L) (hr)
210	7.00	0.051 ± 0.0061	14 ± 2	3.3 ± 0.4
150	5.00	0.035 ± 0.0034	20 ± 2	4.8 ± 0.5
125	4.17	0.039 ± 0.0036	18 ± 2	4.4 ± 0.5
100	3.33	0.026 ± 0.0014	26 ± 1	6.4 ± 0.4
75	2.50	0.009 ± 0.0024	79 ± 29	19 ± 7
50	1.67	0.001 ± 0.0002	990 ± 335	241 ± 82

Given the results of batch experiments, it is apparent that effective utilization of electrochemical reactors to destroy RDX in wastewater will depend on the total surface area available for reaction and the mass transfer characteristics of the reactor. To analyze reactor performance and provide a basis for reactor scale-up, a mass transfer based kinetic rate, k_m , may be used. This rate is defined as $k_m = k(V/A)$, where k is the first

order rate constant, V is the reactor volume, and A is the active electrode surface area (Walsh 1993). The results from transforming the k values of two reactions with constant current density and differing surface areas are given in Table 7. Since the mass-transfer-based rate accounts for differences in total surface area and volume, reactor configurations with similar mass transfer characteristics should have the same k_m value at any scale for a given current density.

Table 7. Comparison of k and k_m values for reactions with differing surface area.

Electrode Surface Area (cm ²)	Current Density (A/m ²)	1 st Order Reaction Coefficient, k (min ⁻¹)	Mass Transfer Based Reaction Coefficient, k_m (m/min)
150	7.00	0.020 ± 0.001	0.0007 ± 0.0001
300	7.00	0.051 ± 0.003	0.0008 ± 0.0001

During initial batch experiments it was observed that reaction kinetics appeared to slow down over time. The apparent cause was a buildup of dissolved solids coating the cathode surface. This reduced the efficiency of the electrodes, effectively reducing the concentration of electrons and hydrogen ions available for reaction (Equation 8). Following from this observation, current reversal was begun for each experiment. By reversing the electrode polarity, scaling on the cathode was electrostatically removed, and electrode efficiency was maintained. Electrode polarity was manually reversed every 20-30 minutes for the duration of the batch experiments.

Comparison of batch electrochemistry with published results

Direct comparisons of observed results to the published literature are problematic because of the wide discrepancy in reactor designs from study to study. Two features of the current study stand out from most published electrochemical treatment experiments. The first is the use of a mixed compartment reactor with no supporting electrolyte. The second is the use of mixed metal oxide/titanium mesh electrodes as both the cathode and anode. Even with the distinct reactor designs used in each study, the mass-transfer-based kinetic rates may be compared as a point of reference (Table 8). The two modifications to reported experiments did not result in a drop in kinetic rates when controlled for mass transfer effects.

Table 8. Observed reaction rates in differing electrochemical reactor configurations.

	Observed	Bonin et al. (2004)	Pehkonen et al. (1999)	Doppalapudi et al. (2001)
Cathode Material	Mixed Metal Oxide / Ti Mesh	Reticulated Vitreous Carbon Foam	Glassy Carbon	Glassy Carbon
Compartment Type	Mixed	Separate	Separate	Separate
Reactor Volume (mL)	500	0.0039	2000	2000
Current Density (A/m²)	7.00	8.66	9.63	9.63
Mass-Transfer-Based Kinetic Rate, $k_m \times 10^5$ (m/min)	84.80	8.03	88.89	32.59

5 Electrochemical Reactor Configuration Studies

Additional electrochemical experiments conducted at a larger scale investigated the feasibility of particular reactor system configurations. A rotating electrode batch reactor was designed to provide better mass transfer from the bulk fluid to the electrode surface. A packed electrode flow reactor was designed to provide a high surface area density in the reactor volume.

Rotating electrode batch reactor

Materials and methods

The rotating electrode sequencing batch reactor was constructed from a 2.7-L acrylic tank and a variable speed mixer. A rotating electrode sequential batch system is shown in Figure 11. The electrode impeller assembly was initially constructed around $\frac{1}{4}$ in. stainless steel tubing that had been electrically insulated with polyolefin shrink tubing (3M Electronics, Austin, TX). Four plates of electrode material 12.7 cm wide by 11.4 cm tall were clamped onto the shaft with nylon cable ties to yield a cathode surface area of 714 cm^2 . Counter electrodes were separated by polypropylene mesh material. During initial testing optimal electrode spacing was determined by increasing or decreasing the amount of polypropylene mesh used to separate counter electrodes and comparing kinetic rates. Following initial testing another electrode setup consisting of eight pairs of electrodes 5.7 cm wide by 11 cm tall arranged in a cross pattern around the mixer shaft was constructed. This setup contained $1,237 \text{ cm}^2$ of active electrode surface area. Electrical connections were made by developing a power commutator for the mixer shaft. The commutator consisted of two sets of carbon brushes aligned with copper collars on the mixer shaft.



Figure 11. Electrochemical batch reactor with rotating electrode impeller and automatic current reversal timer.

Results and discussion

Observations from the small batch experiments (500 ml) led to the development of the larger bench-top reactors designed to approximate full-scale treatment systems. One of the constructed systems was a 2.7-L batch reactor with rotating electrode impellers. Initial experiments in this reactor determined the optimum electrode spacing for RDX treatment. First order reaction coefficients observed in the reactor with varying electrode spacing are summarized in Figure 12. The observed kinetic rate was highest at an electrode spacing of 4 mm, and this spacing was used in all subsequent rotating electrode batch tests.

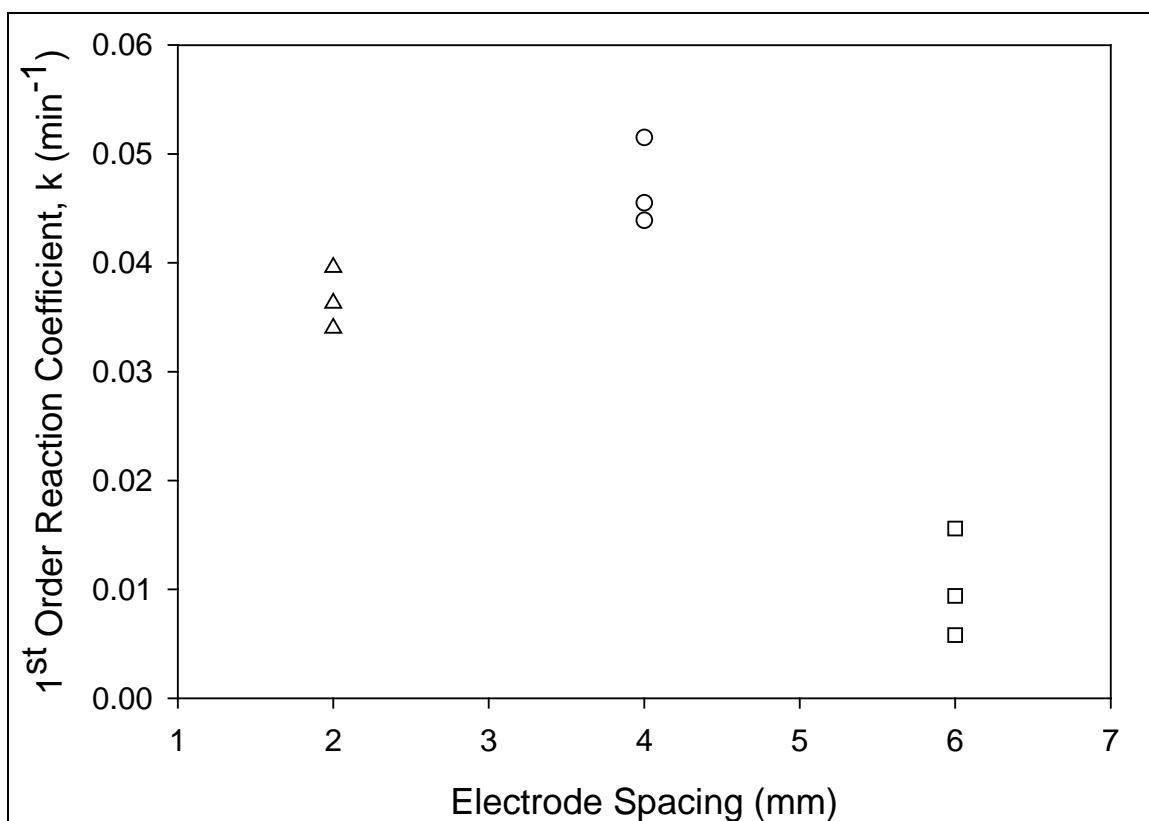


Figure 12. Reaction kinetics profile in a 2.7-L batch reactor with rotating electrode impeller and varying electrode spacing.

Following initial experiments to determine electrode spacing, a higher surface area electrode design was constructed using a cross configuration of electrode plates. Results from testing in this reactor are presented in Figure 13 with half lives and treatment times presented in Table 9. Half lives on the order of 8 minutes were achievable in this reactor indicating a possible treatment time of 2 hr. The main component of operating cost in a full-scale system is expected to be the electrode power requirements. Operating at a current density of 20 A/m^2 , the working voltage was 7 V. Thus the total power required for treatment in this reactor configuration was 0.04 kW-hr/gal.

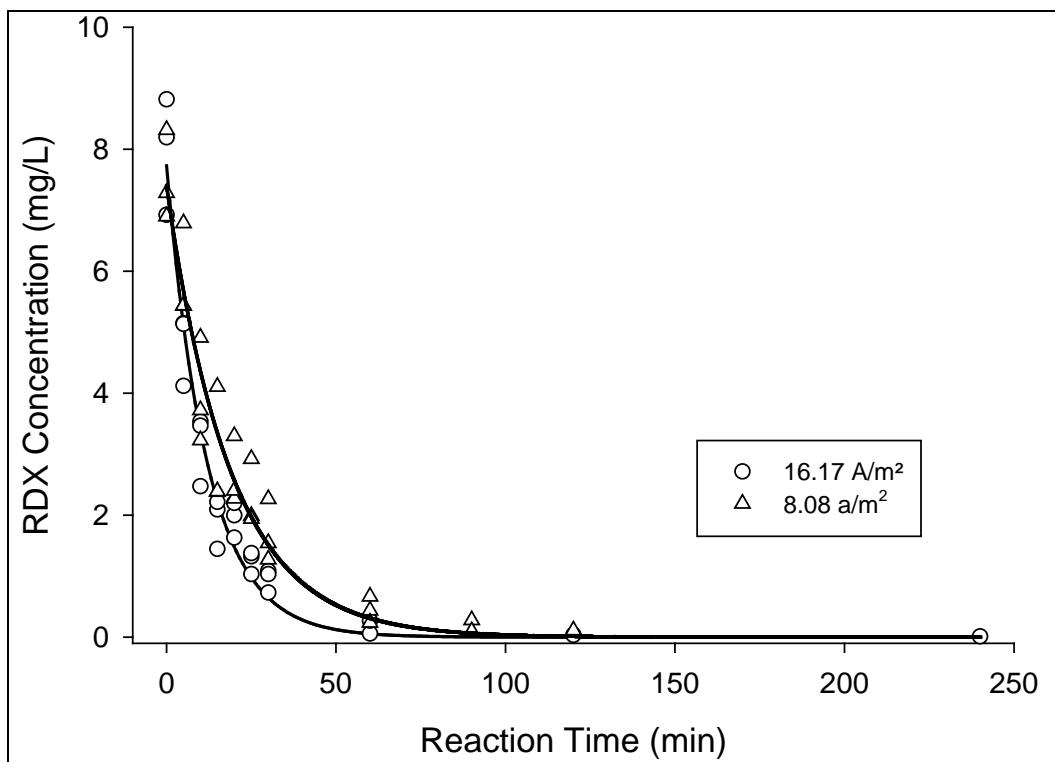


Figure 13. Observed reaction in 2.7-L batch reactor with rotating electrode impeller.

Table 9. Observed kinetic rates and treatment times in a 2.7-L batch reactor with rotating electrode impeller.

Current Density (A/m ²)	1 st Order Kinetic Rate, k (min ⁻¹)	Half Life (min)	Treatment Time (50 mg/L to 2 µg/L) (hr)
8.08	0.053 ± 0.009	13.1 ± 2.0	3.19 ± 0.48
12.12	0.079 ± 0.007	8.8 ± 0.8	2.14 ± 0.18
16.17	0.083 ± 0.012	8.4 ± 1.1	2.04 ± 0.27
20.21	0.086 ± 0.010	8.0 ± 0.8	1.95 ± 0.20

Faster treatment times than the small batch experiments were observed in the rotating electrode batch reactor even though the total reactive surface area per unit volume was less in this configuration. A direct comparison of the mass transfer-based kinetic rates for the small batch experiments and the rotating electrode batch experiments is provided in Figure 14. The k_m was significantly higher at comparable current densities than those observed in the small batch reactors. This indicates that the mass transfer profile of the rotating electrode batch reactor is markedly better, allowing for operation at higher current densities and faster treatment times before reaching mass transfer limitations in the reactor. The mass transfer-based kinetic rate determined by this series of experiments provides a scale-up

parameter that may be used to design full-scale treatment systems for the destruction of RDX in wastewater by sequencing batch reactors with rotating electrode impellers.

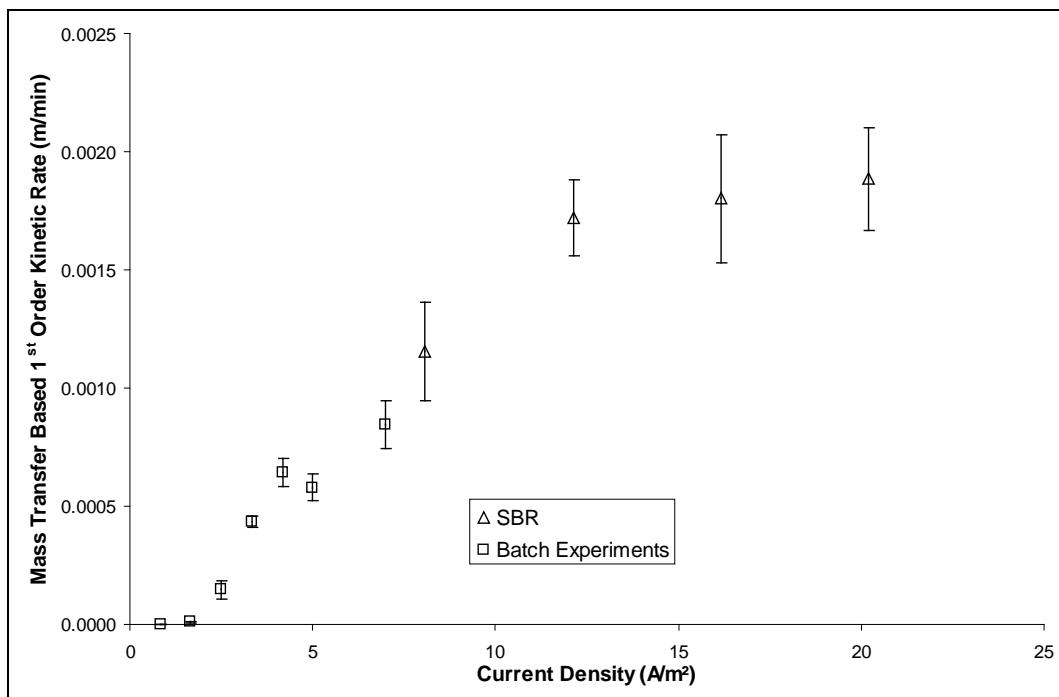


Figure 14. Comparison of the mass-transfer-based kinetic rate of RDX destruction in small batch reactors (SBR) and the rotating electrode batch reactor.

Packed electrode flow reactor

Materials and methods

A continuous flow electrochemical reactor was constructed using a 2-L rectangular acrylic reactor as shown in Figure 15. The reactor is shown in Figure 15 and the design is summarized in Figure 16. The reactor consisted of a 7.62-cm square flow channel 35 cm long. Inside this space, 20 electrode plates (7.62 cm by 23 cm) were placed parallel to the channel. Polypropylene mesh was used between each electrode sheet to maintain electrical isolation in the absence of electrolyte. The final configuration contained 2,156 cm² of cathode surface area. Separate reservoirs were set up for the influent and effluent streams, and a peristaltic pump provided a constant volumetric flow rate through the reactor. Samples were taken at the reactor outlet.

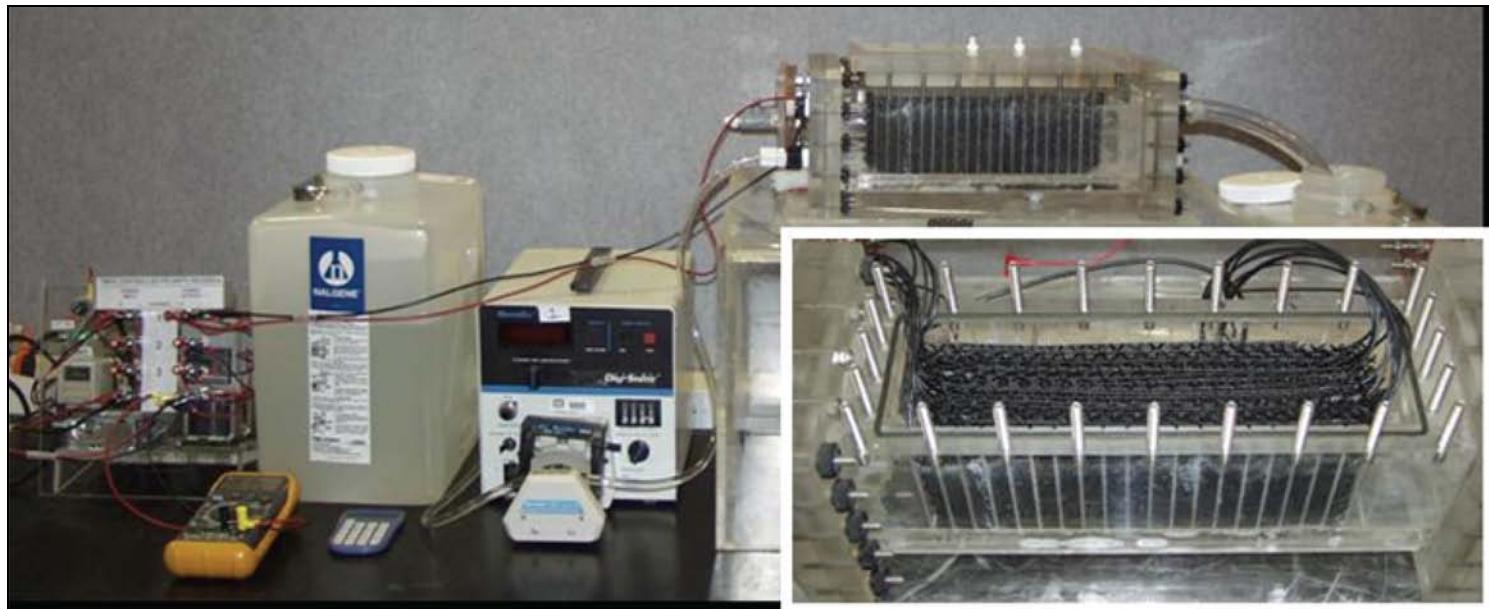


Figure 15. Continuous flow electrochemical reactor packed with electrode plates.

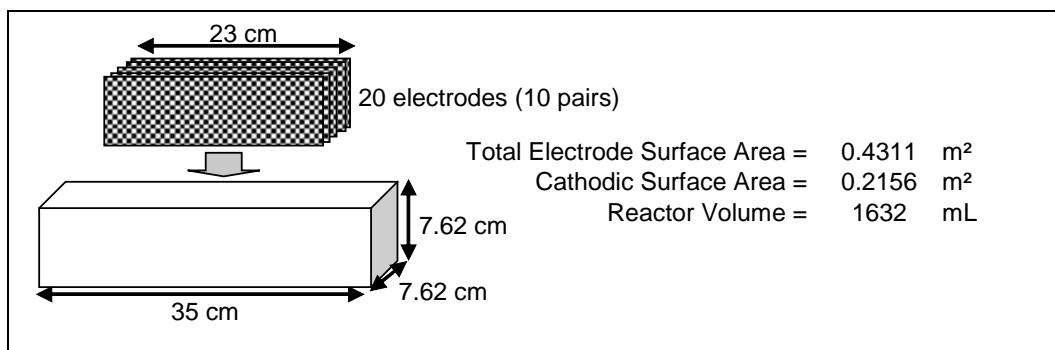


Figure 16. Design configuration for continuous flow electrochemical reactor.

Power was supplied to each bench-top reactor by a single 300V - 3A power supply (Sorensen Inc., San Diego, CA). During batch experiments it was observed that current switching was necessary to prevent buildup of solids on the cathode surface. To that end, a current reversal system was also developed and used for ensuing bench-top experiments. The system used a timer/controller (Autonics Corp., Gyeoungnam, South Korea) to switch mechanical relays (Square D, Palatine, IL) reversing the current polarity of the power source on 20-min intervals.

Results and discussion

Results from testing are detailed in Table 10. The mass-transfer-based kinetic reaction rate for the continuous flow reactor is similar to the rate observed in the small batch reactors, indicating similar mass transfer characteristics. Based on the observed reaction coefficients, treatment from 50 mg/L to less than 2 μ g/L would be accomplished in this reactor at a flow rate of 16 mL/min. This corresponds to a power requirement of 0.03 kW-hr/gal.

Table 10. RDX destruction results from continuous flow electrochemical reactor

Current (A)	Current Density (A/m ²)	Flow Rate (L/min)	k_m (m/min)	95% CI (m/min)	% Destroyed
1.5	6.96	0.129	0.00074	0.00003	71.1%
1.75	8.12	0.129	0.00070	0.00004	69.4%
2	9.28	0.129	0.00061	0.00002	64.1%
2.5	11.60	0.129	0.00067	0.00007	67.4%

6 Combined Electrochemical/Alkaline Batch Studies

Materials and methods

The small batch (500 ml) electrochemical reactor setup (Section 4) was also used to investigate the synergistic effect of electrochemically treating RDX in water under alkaline conditions. This was accomplished by comparing alkaline treatment and electrochemical treatment data generated during earlier experiments to RDX destruction with both high pH and electrochemical reduction. The experimental design is detailed in Table 11. The resulting dataset was a 3² factor designed experiment that could determine if the interaction of electrochemical and alkaline treatments provided more effective treatment than merely the sum of the treatments. Experiments were carried out under every combination of conditions with current densities of 0, 2.14, and 4.29 A/m² and hydroxide concentrations of 10⁻⁴, 0.5, and 100 mM.

Table 11. Experimental design detailed as array of reaction rate constants determined in study of electrochemical/alkaline combined treatment process.

Current Density (A/m ²)	4.29	k ₇	k ₈	k ₉
	2.14	k ₄	k ₅	k ₆
	0.00	k ₁	k ₂	k ₃
	0.0001	0.5	100	

[OH⁻] (mM)

Additional studies were conducted in the rotating electrode batch reactor detailed as part of the bench-top pilot studies. This was done to confirm the results of the small batch studies in a reactor with better mass transfer conditions. These experiments were conducted as a 2² factor designed experiment at current density levels of 11.2 and 22.4 A/m² and hydroxide concentration levels of 10⁻⁵ and 0.5 mM.

Results and discussion

The observed first-order reaction constants for destruction of RDX during combined electrochemical/alkaline treatment are detailed in Figure 17. As expected, RDX is stable at pH 7 unless electrochemical potential is applied. The same remains true at pH 10.67 corresponding to a hydroxide concentration of 0.5 mM. Significant RDX destruction occurs at pH 13 with or without electrochemical potential. At pH 7, the observed reaction rate is $0.035 \pm 0.003 \text{ min}^{-1}$ at a current density of 4.29 A/m^2 . As the pH is increased to 10.67, the observed reaction rate at this current density increases to $0.054 \pm 0.004 \text{ min}^{-1}$, which is greater than the sum of electrochemical treatment at 4.29 A/m^2 and alkaline treatment at pH 10.67. At pH 13, this synergy is no longer observed. In general, the results indicate that moderately increasing the electrolyte pH may significantly decrease the required treatment time for destruction of RDX.

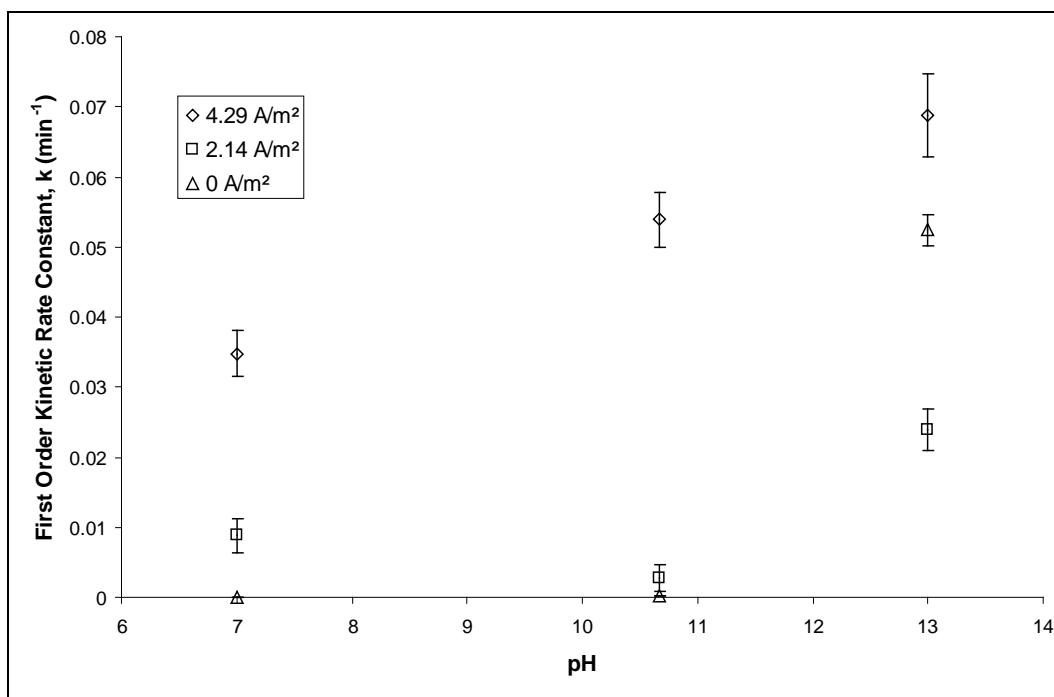


Figure 17. First order kinetic rate constants of RDX destruction for a combined electrochemical/alkaline treatment process in 500-mL reactors (error bars are 95% CI).

Kinetic rate results from the rotating electrode batch reactor are detailed in Figure 18. A direct comparison to the small batch reactor results was made by using the mass transfer-based first order kinetic rate, k_m . In the small batch reactors, moderately alkaline conditions coupled with electrochemical reduction contributed to higher reaction rates than were expected. In the rotating electrode batch reactor, the observed reaction

rates are much slower than expected, and are even lower than those observed at pH 7. The major difference between the reactors is in the mass transfer profile, so the difference in observed reaction rates may be attributable to mass transfer mechanisms. It is beyond the scope of this work to determine the mechanism of synergy that existed in the small batch reactors but not in the larger rotating electrode batch reactor. It is concluded, though, that operating an efficiently designed electrochemical reactor under alkaline conditions is not expected to significantly decrease the required treatment time of RDX wastewater.

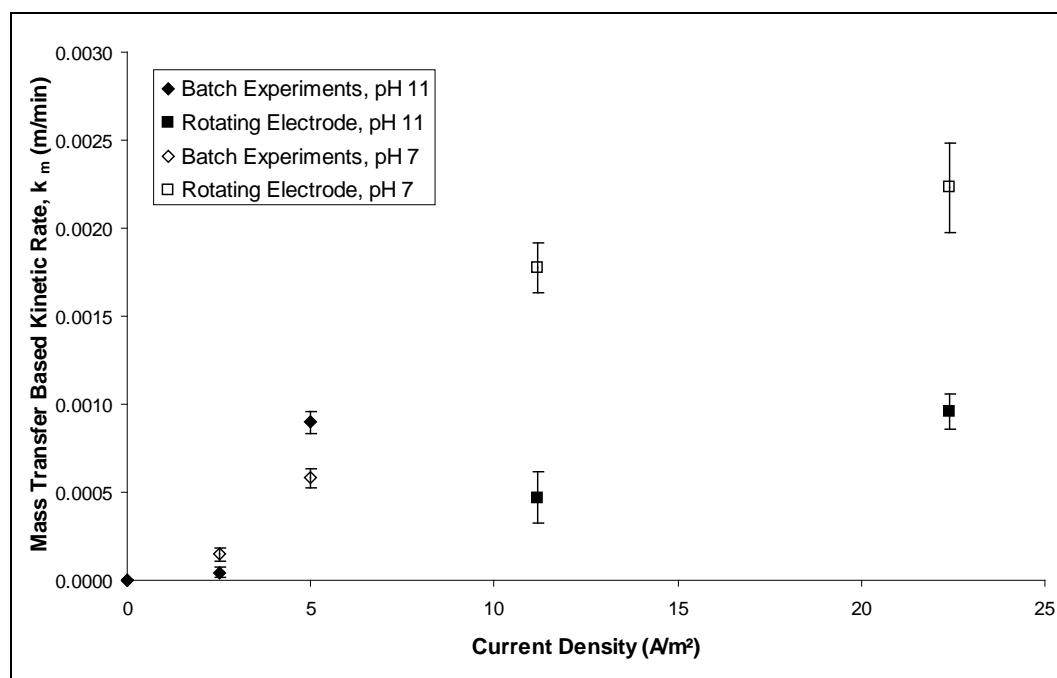


Figure 18. Mass-transfer-based kinetic reaction rates for the destruction of RDX in combined electrochemical/alkaline systems

7 Ultraviolet Oxidation Batch Studies

Materials and methods

Studies were also undertaken to determine the rate of RDX decay under ultraviolet oxidation. The reactor setup is illustrated in Figure 19, and a photo of the reactor during testing is shown in Figure 20. The basic components were a 1-L photochemical reactor with immersion type lamps and power supplies of both 200 W and 450 W (Ace Glass, Vineland, NJ). RDX-laden water circulated between the photochemical reactor and a 1-L mixed reservoir by means of a peristaltic pump. The total volume of process wastewater treated in each experiment was 2 L. Samples were removed at defined intervals from the reactor vessel and analyzed by HPLC/UV for the remaining RDX concentration as well as the recognized breakdown products MNX, DNX, and TNX.

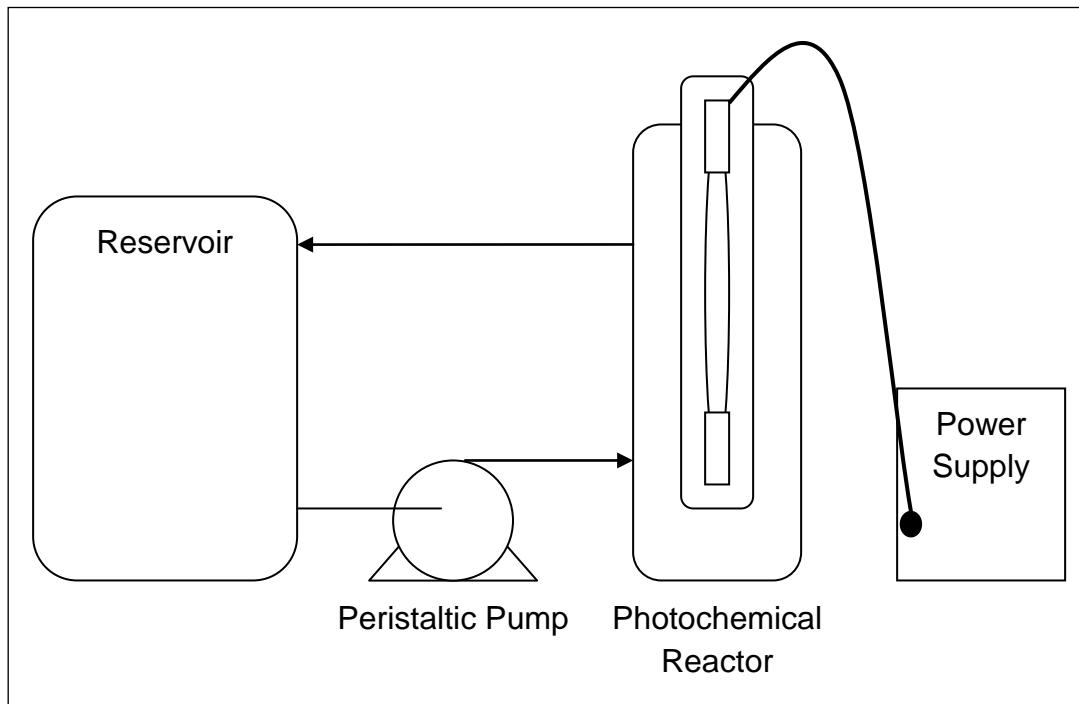


Figure 19. Experimental setup for determination of decay rates for ultraviolet oxidation of RDX in HSAAP industrial wastewater.

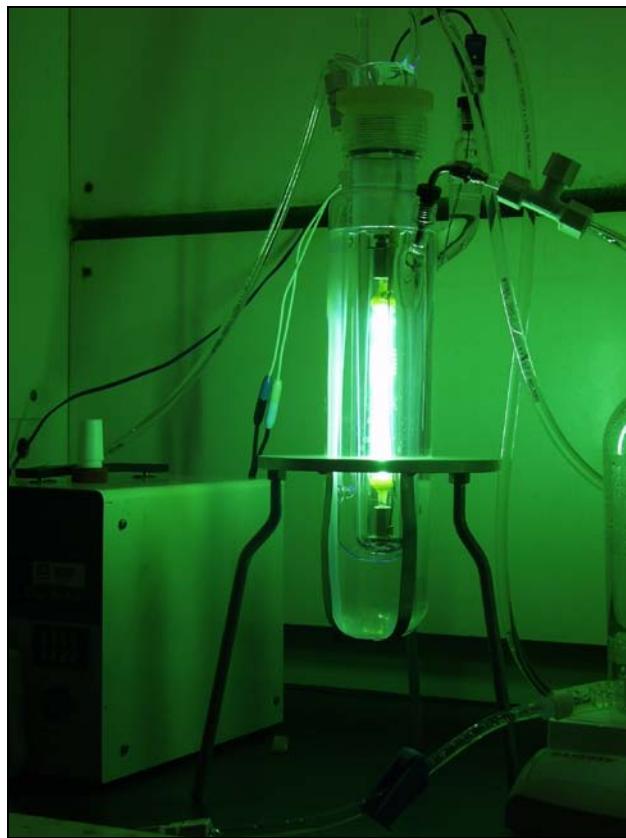


Figure 20. Photochemical reactor used to test UV oxidation of RDX in HSAAP wastewater.

Kinetic rates results and discussion

Ultraviolet oxidation of pure solutions of RDX, neglecting absorption of photons by reaction byproducts, may be expressed as

$$\frac{dC}{dt} = -I\varphi[1 - e^{-2.803b} C]$$

Equation 11. Reaction rate of ultraviolet oxidation of pure RDX in solution.

where C is the instantaneous concentration of RDX in the reactor, t is the reaction time, I is the light intensity in einsteins/L-sec, φ is the quantum yield of RDX in moles/Einstein, ε is the molar absorptivity of RDX (5000 M/cm at 254 nm), and b is the path length in centimeters. For relatively low RDX concentrations, in this case starting concentrations on the order of 45 μ M, a first order Taylor approximation of the rate law may be used such that

$$\frac{dC}{dt} = -I\varphi \cdot 2.303 \cdot \varepsilon b C$$

Equation 12. Reaction rate for low concentrations of RDX utilizing a first order Taylor approximation.

In the reactor setup used, UV oxidation is occurring in the reactor, but not in the reservoir. In light of this, the reaction kinetics must be determined by developing a design equation for the reactor based on the mass balance around the photochemical reactor and reservoir, respectively:

$$\frac{dC_2}{dt} = \frac{v}{V_2} (C_1 - C_2)$$

$$\frac{dC_1}{dt} = \frac{v}{V_1} (C_2 - C_1)$$

Equation 13. Separation of reaction kinetics of photochemical reactor and reservoir.

where C_1 and C_2 are the instantaneous RDX concentrations in the photochemical reactor and reservoir, respectively, V_1 and V_2 are the volumes of the reactor and reservoir, respectively, t is the reaction time, and v is the volumetric flow rate of the circulation pump. Placing these mass balances in a system with the assumed rate law and solving yields a design equation of

$$C = C_0 \exp \left[-\frac{2.303 \cdot I \cdot b}{1 + 2.303 \cdot I \cdot b} \cdot \frac{\tau_1}{\tau_1 - \tau_2} t \right]$$

Equation 14. Design equation for the reaction rate of RDX in a photochemical reactor.

where τ_1 and τ_2 are the average residence times of the reactor and reservoir, respectively, defined as $\tau = V/v$. In any given reactor setup, the quantity $2.303 \cdot I \varphi b \varepsilon$ will be a reaction constant analogous to the first order reaction constant k . By estimating k through a least squares fit to data, the quantum yield of the reaction may then be calculated from the known quantities of intensity, path length, and absorptivity. The observed kinetic rate may be used to make comparisons within a single reactor, while additional comparisons may be made by changing the path length, etc. to reflect changing reactor conditions. Since one underlying

assumption is that only RDX contributes to absorptivity in the reactor, the calculated quantum yield will represent a lower limit estimate.

The decay of RDX with time under UV oxidation is shown in Figure 21. The apparent first order reaction constants of RDX decay are detailed with the calculated half lives under both 200 W and 450 W lamps in Table 12. There is no significant difference between the reaction rates under the different lamp wattages. In each case the half life of RDX destruction is on the order of one minute. Assuming a reduction in RDX from 50 mg/L to 2 μ g/L, the total treatment time under these conditions would be 14 minutes. The main component of the ultimate operating cost in an ultraviolet oxidation system will result from energy costs. In the reactor configuration tested, the total energy input was 0.09 kW-hr/gal.

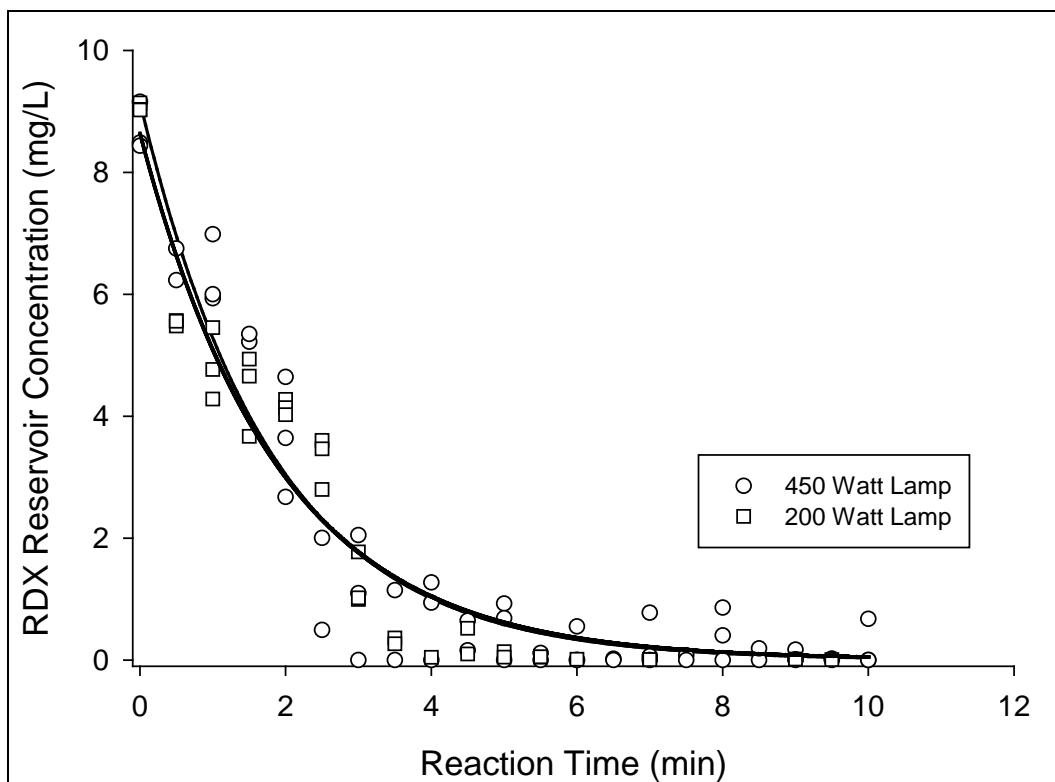


Figure 21. Disappearance of RDX with time in a UV oxidation batch reactor.

Table 12. Reaction constants and half lives of UV oxidation.

Lamp Power	1st Order Reaction Constant, k (min^{-1})	Std Error of k (min^{-1})	Half Life (min)
200 W	0.90	0.04	0.77
450 W	0.84	0.04	0.82

8 Comparison of Technologies Investigated

This effort undertook the bench scale testing of four possible destructive treatment technologies for RDX in an industrial process wastewater: alkaline hydrolysis, direct electrochemical reduction, alkaline-assisted electrochemical reduction, and ultraviolet oxidation. Four of the investigated configurations are summarized in Table 13. The alkaline-assisted electrochemical reduction configuration does not warrant further investigation at this point, since no benefit was observed in adding alkalinity to the system in the scale-up reactor. At this stage of development, the main points of comparison are the effectiveness and operating cost of the proposed systems. Total operating costs include factors such as maintenance that are not addressed during a bench scale evaluation, but a preliminary analysis may be made based on the major expected input cost. For alkaline hydrolysis, this would be the chemical cost of pH adjustment. For UV oxidation and electrochemical reduction, this would be the energy cost. Of all of the configurations investigated, UV oxidation had the shortest treatment times. The energy costs associated with UV, though, were roughly three times the costs associated with electrochemical reduction. Alkaline hydrolysis exhibited the highest potential operating costs, although it has the advantage of being the simplest system available. Adding base does not require the customized equipment that electrochemical reduction or UV oxidation would.

Given the analysis and laboratory testing performed on this project, four viable technologies have been investigated for the destruction of RDX in the HSAAP waste stream. One technology (alkaline hydrolysis) requires no custom equipment, but exhibits markedly higher estimated operating costs. The remaining three technologies exhibit lower estimated operating costs, but are more complicated processes requiring specialized equipment. Of these three, UV oxidation has much higher energy input costs. In order to determine the best option, pilot scale reactors should be built that allow for a firmer evaluation of technology effectiveness, operating cost, and capital cost. Ultraviolet oxidation may be ruled out in preference of direct electrochemical reduction based on energy input requirements. The resulting study would be a pilot evaluation of alkaline hydrolysis and direct electrochemical reduction in both the batch and continuous modes.

Table 13. Comparison of investigated technologies for the treatment of RDX in wastewater.

Process Description	Observed Half Life (min)	Estimated Input Energy (kW-hr/1000 gal)	Estimated Energy Cost at \$0.10 per kW-hr (\$/1000 gal)	Estimated Chemical Cost (\$/1000 gal)	Estimated Chemical/ Utilities Cost (\$/1000)
Alkaline Hydrolysis – pH 13	22	n/a	n/a	20	20
Direct Electrochemical Reduction – <i>Batch</i> Reactor	8	40	4	n/a	4
Direct Electrochemical Reduction – <i>Flow Through</i> Reactor	7.3	30	3	n/a	3
Ultraviolet Oxidation	0.8	90	9	n/a	9

9 Conclusions

The objective of this work was to evaluate potential primary treatment systems for the destruction of RDX in HSAAP waste streams. Several treatment options were surveyed, and this effort undertook the bench scale testing of four possible destructive treatment technologies for RDX in an industrial process wastewater: alkaline hydrolysis, direct electrochemical reduction, alkaline-assisted electrochemical reduction, and ultraviolet oxidation. At this stage of development, the main points of comparison are the effectiveness and operating cost of the proposed systems. Alkaline hydrolysis exhibited the highest potential operating costs, although it has the advantage of being the simplest system available. Adding base does not require the specialized equipment that electrochemical reduction or UV oxidation would. Between electrochemical and UV technologies, direct electrochemical reduction is preferable given the much lower energy input required.

In order to determine the best option for a full-scale treatment plant, pilot scale reactors should be built that allow for a more firm evaluation of technology effectiveness, operating cost, and capital cost. Ultraviolet oxidation may be ruled out in preference of direct electrochemical reduction because of the high energy requirements of UV lights. Alkaline hydrolysis merits further study given the potential for much lower capital costs. The resulting study would be a pilot evaluation of two direct electrochemical reduction configurations and one alkaline hydrolysis configuration. Information developed during the pilot will lead to a full economic analysis of alternative primary treatment systems to remove RDX from a process waste stream.

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Appendix A. Supporting Data for Alkaline Hydrolysis

Table A- 1. Reaction kinetic data for alkaline hydrolysis of RDX at pH 11.

pH	Hydroxide	1 st Order Kinetic	Half	Treatment
	Concentration (mM)	Rate Constant (hr ⁻¹)	Life (hr)	Time (hr)
11.00	1	0.012	57.8	517.9

Reaction Time (min)	RDX		RDX Concentration R2 (mg/L)
	Concentration R1 (mg/L)	Concentration R2 (mg/L)	
0	0.988		1.397
120	0.901	0.874	1.101
240	0.831	0.836	0.8
1440	0.716	0.731	0.742
2880	0.516	0.519	0.598
4320	0.444	0.403	0.46
5760	0.415	0.362	0.403
7200	0.332	0.339	0.34
8640	0.25	0.274	0.278
10080	0.191	0.237	0.34
11520	0.216	0.234	0.179
12960	0.08	0.096	0.166
14400	0.081	0.154	0.18
15840	0.049	0.161	0.124
17280	0.026	0.08	0.038
18720	0.042	n.a.	0.065
20160	0.014	0.051	0.014

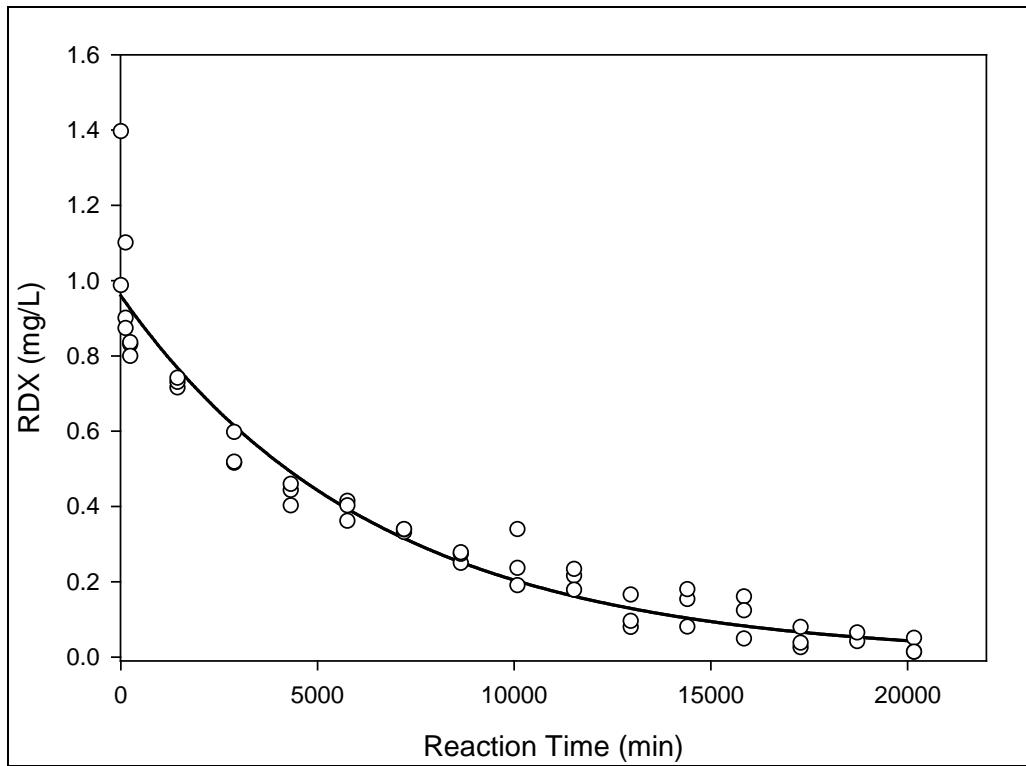


Table A- 2. Reaction kinetic data for alkaline hydrolysis of RDX at pH 12.

pH	Hydroxide	1 st Order Kinetic	Half	Treatment
	Concentration (mM)	Rate Constant (hr ⁻¹)	Life (hr)	Time (hr)
12.00	10	0.156	4.4	39.8

Reaction Time (min)	RDX R1 (mg/L)	RDX R2 (mg/L)	RDX R2 (mg/L)
9	7.700	7.737	7.211
30	8.046	8.671	8.124
60	7.415	8.805	8.918
90	9.142	9.001	8.817
120	8.639	9.313	9.135
180	6.297	7.117	5.493
240	5.593	5.649	4.223
300	5.304	4.953	4.116
360	3.879	3.998	3.652
420	2.552	2.507	3.720
540	1.675	2.601	1.636
660	0.909	1.123	0.443
780	1.404	1.439	0.542
900	1.098	1.545	0.371
1020	0.275	0.372	0.157
1140	0.207	0.284	0.127
1260	0.126	0.170	0.095
1380	0.332	0.115	0.090
1560	0.075	0.071	0.082
1740	0.019	0.053	0.007
1980	0.019	n.a.	0.061
2220	n.a.	n.a.	n.a.
2460	n.a.	n.a.	n.a.
2700	n.a.	n.a.	0.033
2940	0.009	n.a.	0.020

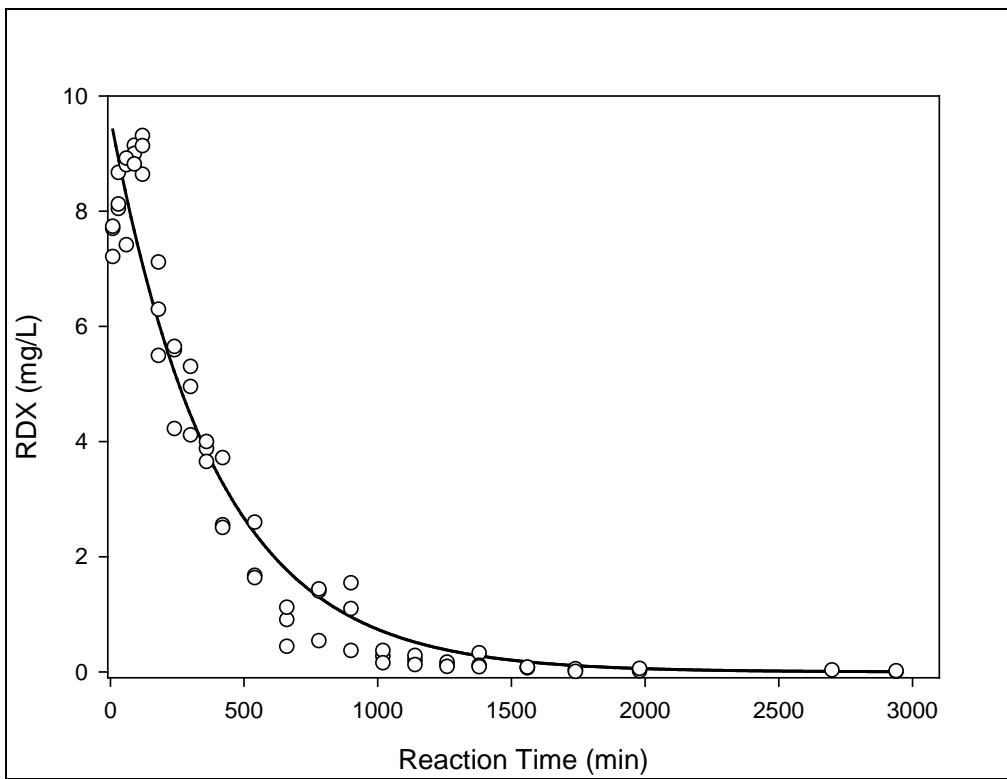


Table A- 3. Reaction kinetic data for alkaline hydrolysis of RDX at pH 12.5.

pH	Hydroxide Concentration (mM)	1 st Order Kinetic Rate Constant (hr ⁻¹)	Half Life (hr)	Treatment Time (hr)
12.50	32	0.504	1.4	12.3

Reaction Time (min)	RDX R1 (mg/L)	RDX R2 (mg/L)	RDX R2 (mg/L)
0	8.943	8.017	8.709
30	6.302	7.903	7.771
60	5.986	5.930	5.166
90	5.438	5.128	5.258
120	0.544	2.963	0.451
180	2.022	2.104	2.000
240	1.201	1.231	1.190
300	0.684	0.694	0.612
360	0.152	0.378	0.300
420	0.376	0.754	4.251
540	0.015	n.a.	n.a.
660	n.a.	n.a.	n.a.
780	0.030	n.a.	n.a.
900	0.008	n.a.	n.a.
1020	n.a.	n.a.	n.a.
1140	0.013	n.a.	n.a.
1260	0.011	n.a.	n.a.
1380	n.a.	n.a.	0.000

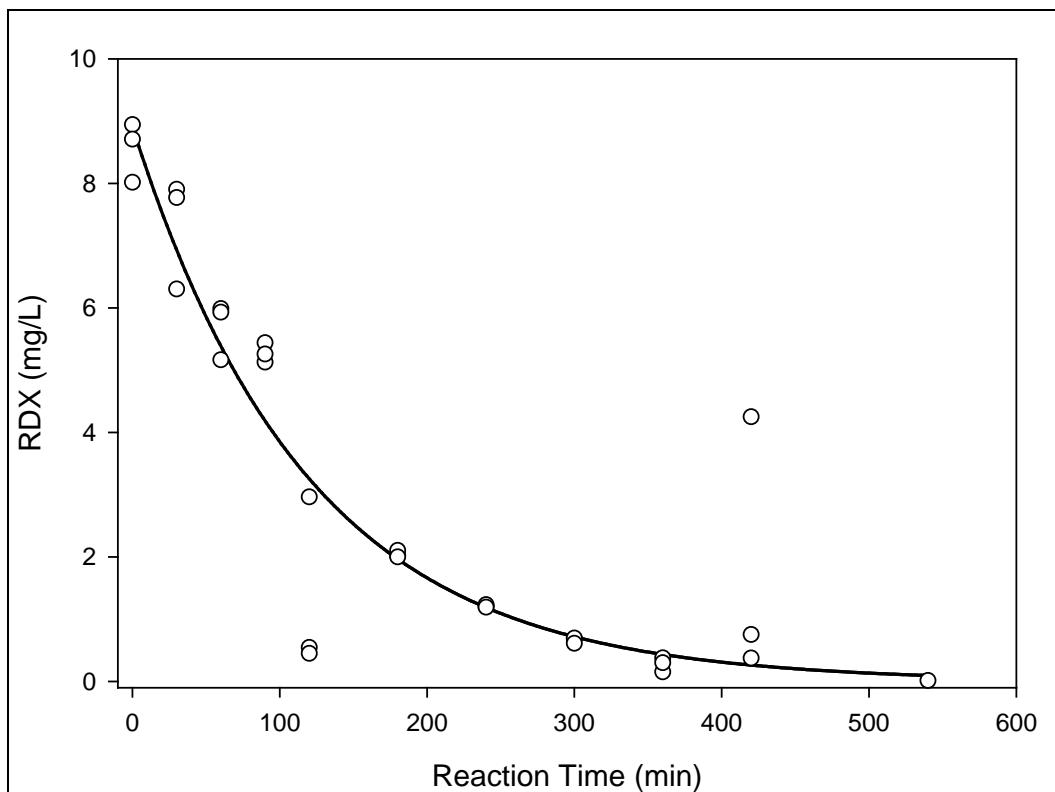


Table A- 4. Reaction kinetic data for alkaline hydrolysis of RDX at pH 13.

pH	Hydroxide	1 st Order Kinetic	Half	Treatment
	Concentration (mM)	Rate Constant (hr ⁻¹)	Life (hr)	Time (hr)
13.00	100	1.61	0.4	3.9

Reaction Time (min)	RDX	RDX	RDX
	Concentration R1 (mg/L)	Concentration R2 (mg/L)	Concentration R2 (mg/L)
0	6.503	6.879	6.879
15	4.726	4.727	4.770
30	3.121	3.082	3.198
45	2.024	2.020	2.042
60	1.315	1.352	1.299
90	0.513	0.451	0.529
120	0.190	0.206	0.150
180	n.a.	n.a.	n.a.
240	n.a.	n.a.	n.a.
300	n.a.	n.a.	n.a.
360	n.a.	n.a.	n.a.

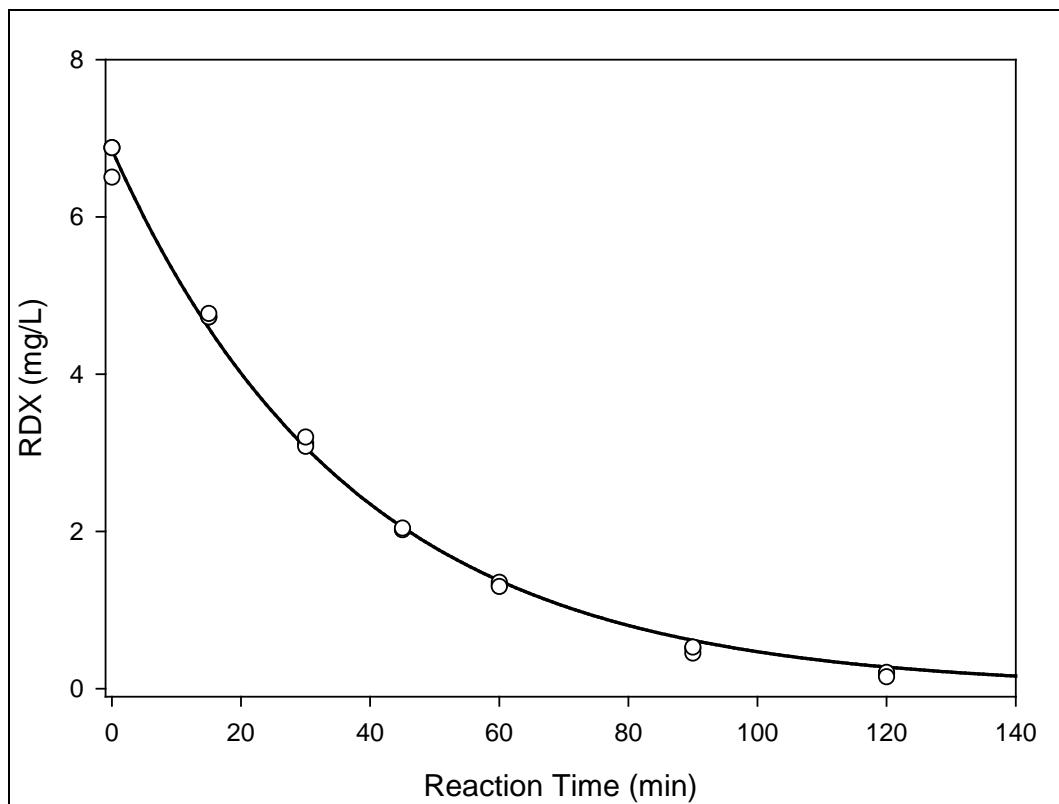
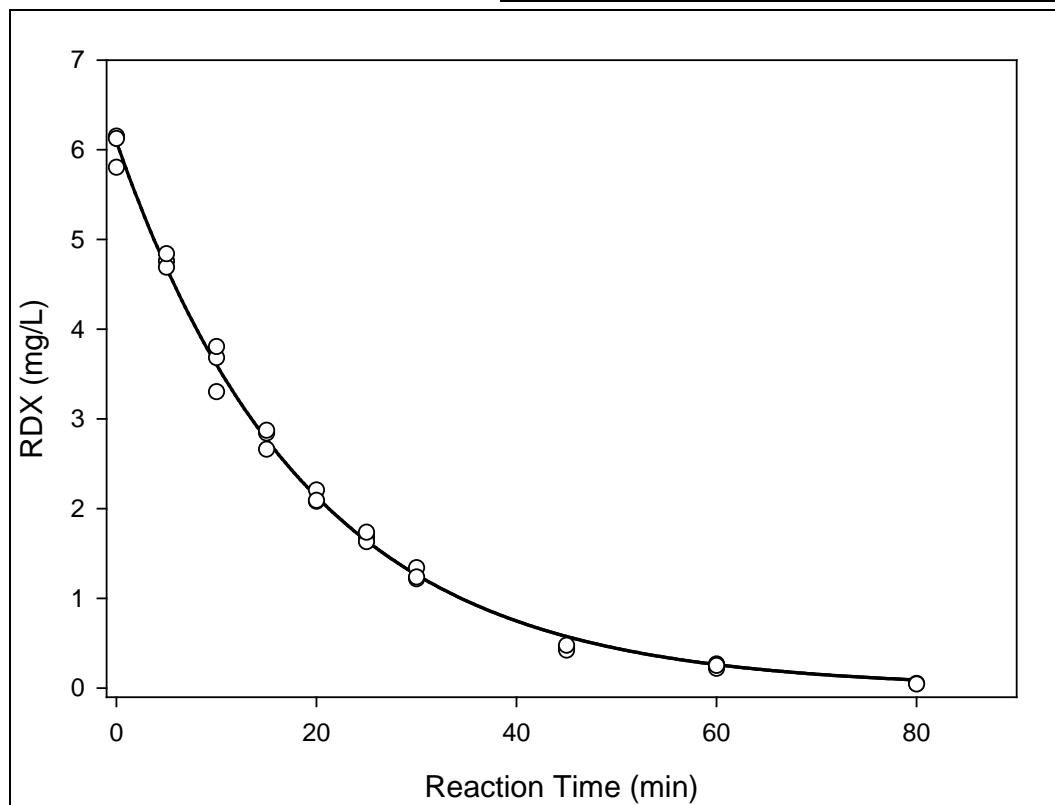


Table A- 5. Reaction kinetic data for alkaline hydrolysis of RDX at pH 13.3.

Hydroxide pH	Concentration (mM)	1 st Order Kinetic Rate Constant (hr ⁻¹)	Half Life (hr)	Treatment Time (hr)
13.30	200	3.14	0.2	2.0

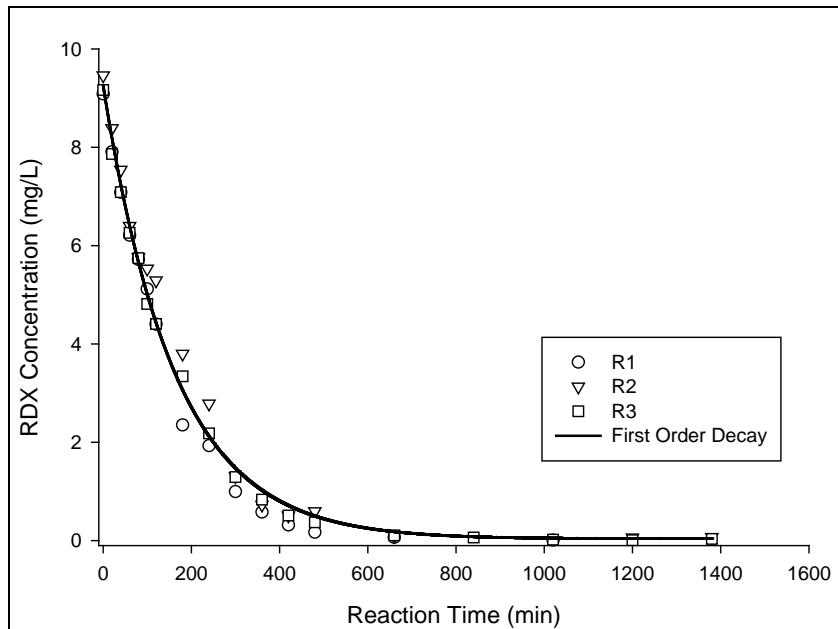
Reaction Time (min)	RDX R1 (mg/L)	RDX R2 (mg/L)	RDX R2 (mg/L)
0	6.151	5.805	6.124
5	4.760	4.690	4.841
10	3.682	3.303	3.805
15	2.842	2.662	2.872
20	2.208	2.081	2.091
25	1.684	1.632	1.736
30	1.217	1.341	1.238
45	0.448	0.422	0.477
60	0.269	0.220	0.251
80	0.052	0.045	n.a.
100	n.a.	n.a.	n.a.
120	n.a.	n.a.	n.a.
150	n.a.	n.a.	n.a.
180	n.a.	0.008	0.018
210	n.a.	n.a.	n.a.
240	n.a.	n.a.	n.a.



Appendix B. Supporting Data for Electrochemical RDX Reduction

Table B- 1. . Reaction kinetic data for electrochemical reduction of RDX, experiment #1.

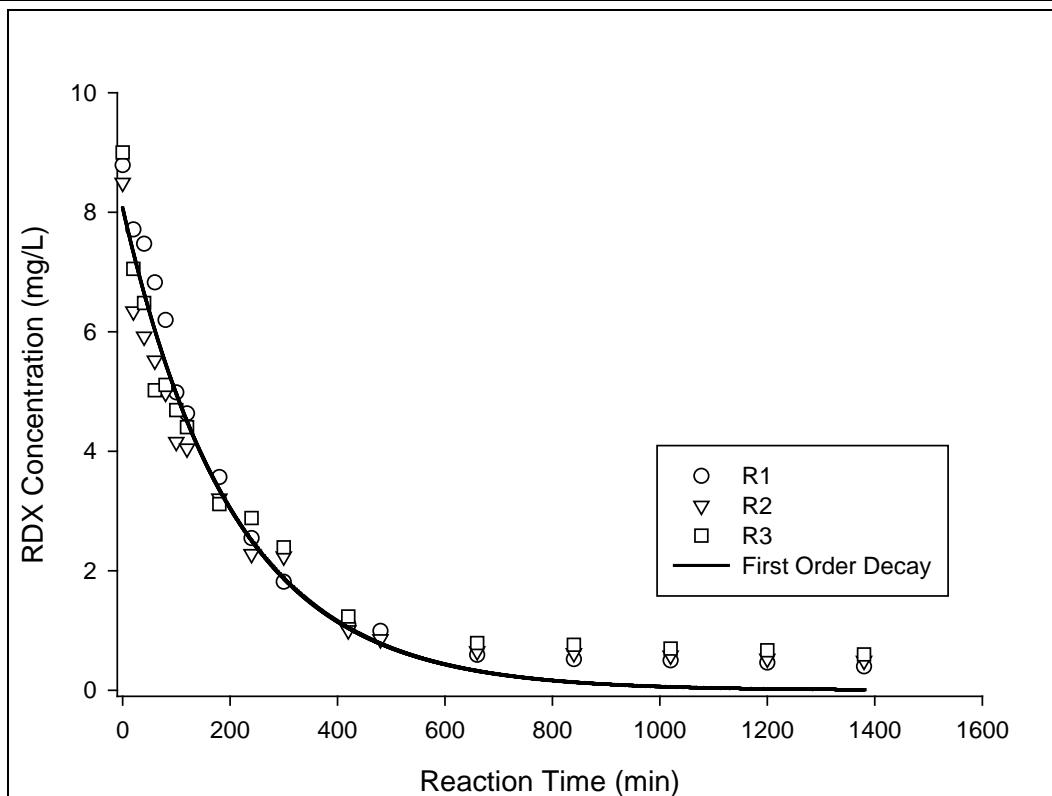
Experimental Run : 1	
Electrode width =	1.27 cm
Submerged depth =	8.00 cm
Cathode Area =	25.01 cm ²
Current =	20 mA
Current Density =	8.0 A/m ²
1 st Order Reaction Coefficient, k = 0.0061 min ⁻¹	
Standard Deviation of k = 0.0002 min ⁻¹	
95% Confidence Interval Of k = 0.0001 min ⁻¹	
Mass Transfer Based Reaction Coefficient, k _m = 0.000040 m/min	
95% Confidence Interval Of k _m = 0.000011 m/min	



Reaction Time (min)	Reactor 1		Reactor 2		Reactor 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	9.085	n.a.	9.459	n.a.	9.164	n.a.
20	7.905	n.a.	8.386	n.a.	7.863	n.a.
40	7.084	n.a.	7.539	n.a.	7.087	n.a.
60	6.21	0.0894	6.396	n.a.	6.258	n.a.
80	5.718	n.a.	5.759	0.1237	5.746	n.a.
100	5.115	0.1468	5.528	n.a.	4.814	n.a.
120	4.4	n.a.	5.289	n.a.	4.406	n.a.
180	2.351	n.a.	3.796	0.0722	3.341	n.a.
240	1.931	n.a.	2.785	n.a.	2.181	n.a.
300	0.995	0.0956	1.305	0.1268	1.292	0.0892
360	0.579	0.0637	0.727	0.0609	0.834	0.0574
420	0.316	0.0391	0.508	n.a.	0.509	n.a.
480	0.17	0.0264	0.594	n.a.	0.373	0.0317
660	0.065	n.a.	0.093	0.0043	0.106	n.a.
840	n.a.	n.a.	n.a.	n.a.	0.063	n.a.
1020	0.008	n.a.	n.a.	n.a.	0.02	n.a.
1200	n.a.	n.a.	0.059	n.a.	0.008	n.a.
1380	n.a.	n.a.	0.068	n.a.	0.033	n.a.

Table B-2. Reaction kinetic data for electrochemical reduction of RDX, experiment #2.

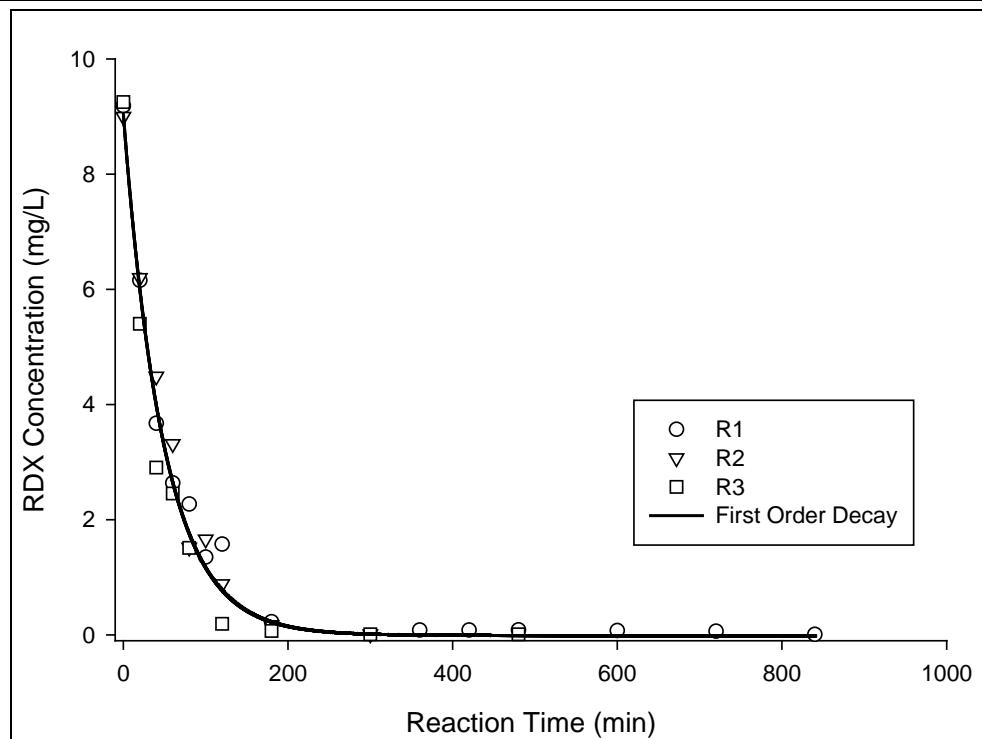
Experimental Run : 2		1 st Order Reaction Coefficient, $k = 0.0049 \text{ min}^{-1}$
Electrode width =	1.27 cm	Standard Deviation of $k = 0.0003 \text{ min}^{-1}$
Submerged depth =	8.00 cm	95% Confidence Interval Of $k = 0.0001 \text{ min}^{-1}$
Cathode Area =	25.01 cm ²	Mass Transfer Based Reaction Coefficient, $k_m = 0.000060 \text{ m/min}$
Current =	50 mA	95% Confidence Interval Of $k_m = 0.000017 \text{ m/min}$
Current Density =	20.0 A/m ²	



Reaction Time (min)	Reactor 1		Reactor 2		Reactor 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	8.788	0.0816	8.491	n.a.	9.001	n.a.
20	7.709	n.a.	6.34	n.a.	7.052	n.a.
40	7.471	n.a.	5.917	n.a.	6.48	n.a.
60	6.823	0.1063	5.517	n.a.	5.021	n.a.
80	6.195	n.a.	4.978	0.0522	5.109	n.a.
100	4.982	0.0781	4.154	n.a.	4.688	n.a.
120	4.63	n.a.	4.044	n.a.	4.402	n.a.
180	3.565	n.a.	3.209	0.1759	3.117	n.a.
240	2.545	n.a.	2.278	n.a.	2.883	n.a.
300	1.815	n.a.	2.24	n.a.	2.391	n.a.
420	1.095	n.a.	1.005	n.a.	1.234	0.0143
480	0.993	0.0089	0.853	0.0077		
660	0.591	n.a.	0.652	n.a.	0.789	n.a.
840	0.518	n.a.	0.62	n.a.	0.762	0.0055
1020	0.499	n.a.	0.579	n.a.	0.699	n.a.
1200	0.462	0.0394	0.528	0.0042	0.669	n.a.
1380	0.398	n.a.	0.493	0.0044	0.599	n.a.

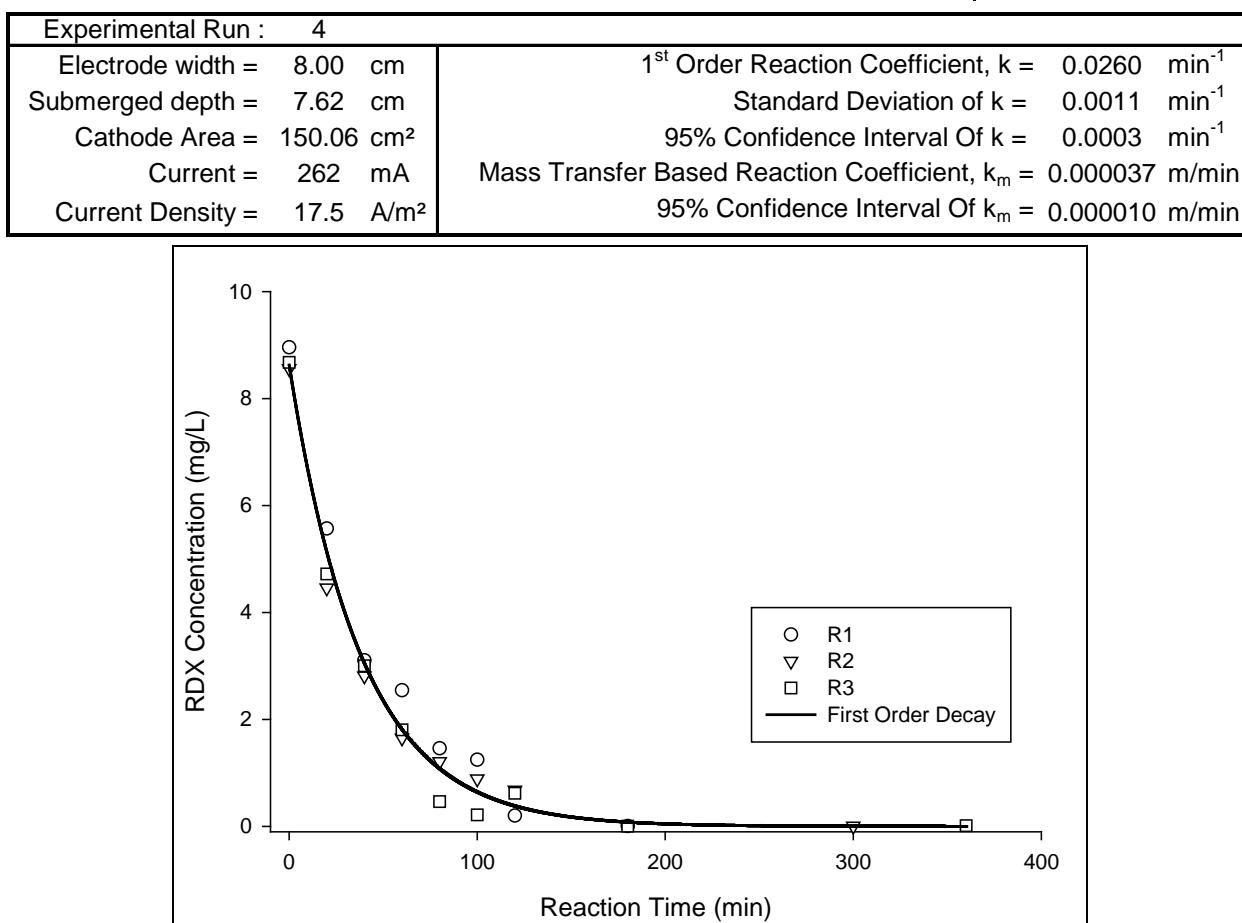
Table B- 3. Reaction kinetic data for electrochemical reduction of RDX, experiment #3.

Experimental Run : 3		1 st Order Reaction Coefficient, $k = 0.0204 \text{ min}^{-1}$
Electrode width =	8.00 cm	Standard Deviation of $k = 0.0008 \text{ min}^{-1}$
Submerged depth =	7.62 cm	95% Confidence Interval Of $k = 0.0002 \text{ min}^{-1}$
Cathode Area =	150.06 cm ²	Mass Transfer Based Reaction Coefficient, $k_m = 0.000027 \text{ m/min}$
Current =	105 mA	95% Confidence Interval Of $k_m = 0.000007 \text{ m/min}$
Current Density =	7.0 A/m ²	



Reaction Time (min)	Reactor 1		Reactor 2		Reactor 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	9.185	n.a.	8.996	0.1232	9.25	0.0908
20	6.156	n.a.	6.199	n.a.	5.401	n.a.
40	3.673	0.2632	4.487	0.2154	2.906	n.a.
60	2.638	0.2975	3.315	n.a.	2.455	n.a.
80	2.27	n.a.	1.517	0.3422	1.512	1.1969
100	1.351	n.a.	1.66	0.0745	n.a.	0.8041
120	1.574	0.2585	0.884	n.a.	0.194	0.7371
180	0.228	0.1345	0.173	0.1683	0.068	0.1114
240	n.a.	0.11	n.a.	0.1077	n.a.	0.1082
300	n.a.	0.1027	0.01	0.0899	0.011	0.1146
360	0.083	n.a.	n.a.	n.a.	n.a.	0.0039
420	0.083	n.a.	n.a.	n.a.	n.a.	0.0072
480	0.085	n.a.	n.a.	n.a.	0.012	n.a.
600	0.074	n.a.	n.a.	0.0066	n.a.	n.a.
720	0.062	n.a.	n.a.	n.a.	n.a.	n.a.
840	0.008	n.a.	n.a.	n.a.	n.a.	n.a.

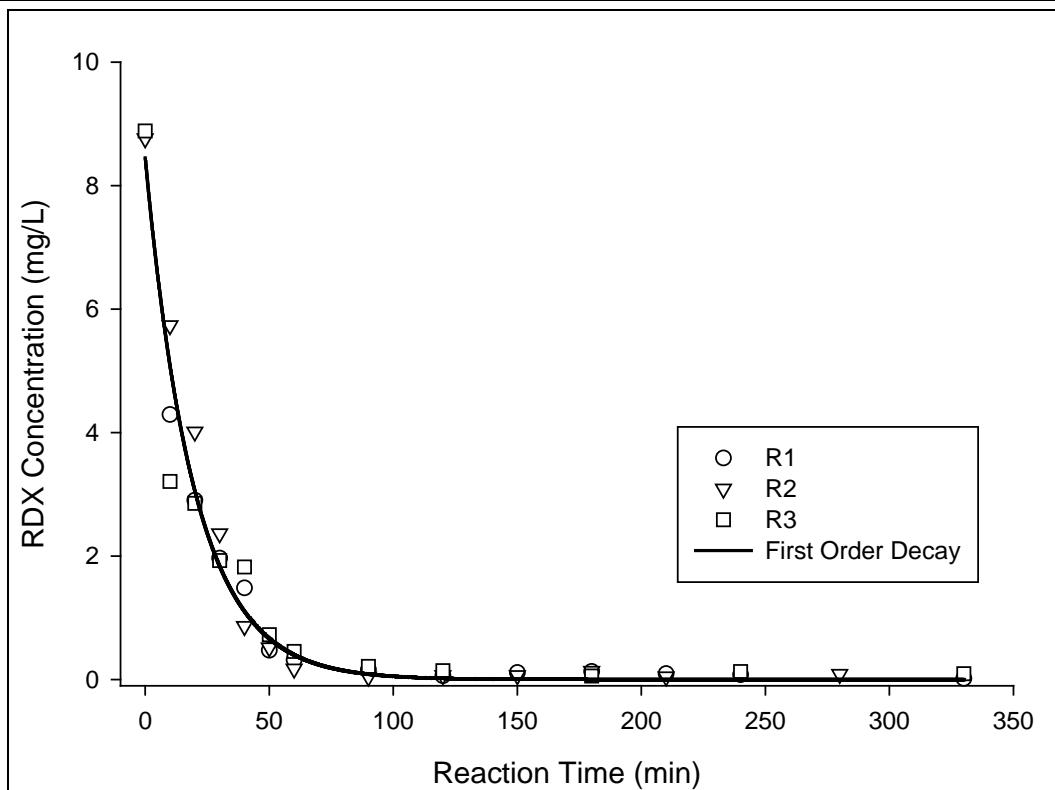
Table B- 4. Reaction kinetic data for electrochemical reduction of RDX, experiment #4



Reaction Time (min)	Reactor 1		Reactor 2		Reactor 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	8.957	n.a.	8.558	1.2756	8.676	1.4573
20	5.569	n.a.	4.457	1.5286	4.721	1.4372
40	3.106	0.1496	2.812	1.5018	3.004	1.3961
60	2.545	n.a.	1.653	1.3578	1.807	1.6239
80	1.459	1.4657	1.211	1.1478	0.464	1.4966
100	1.245	1.5411	0.887	1.1927	0.217	1.5871
120	0.201	1.3218	0.679	1.5864	0.621	1.4844
180	0.006	0.0868	n.a.	0.0462	0.006	0.0127
300	n.a.	0.0045	0.006	0.0112	n.a.	n.a.
360	n.a.	n.a.	n.a.	0.0326	0.013	0.0052

Table B- 5. Reaction kinetic data for electrochemical reduction of RDX, experiment #5

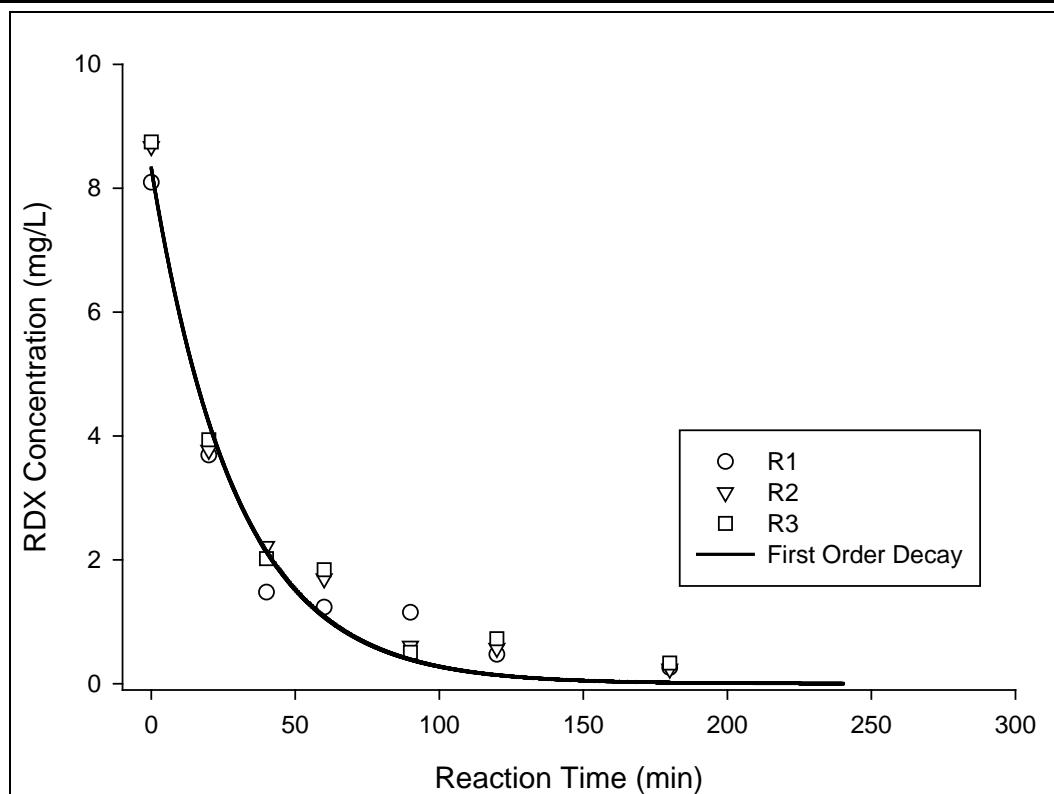
Experimental Run : 5		1 st Order Reaction Coefficient, k = 0.051 min ⁻¹	
Electrode width =	8.00 cm	Standard Deviation of k =	0.003 min ⁻¹
Submerged depth =	7.62 cm	95% Confidence Interval Of k =	0.006 min ⁻¹
Cathode Area =	300.11 cm ²	Mass Transfer Based Reaction Coefficient, k _m =	0.0008 m/min
Current =	210 mA	95% Confidence Interval Of k _m =	0.0001 m/min
Current Density =	7.0 A/m ²		



Reaction Time (min)	Reactor 1		Reactor 2		Reactor 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	0	n.a.	8.76	n.a.	8.885	n.a.
10	4.29	0.1316	0.094	n.a.	0.174	n.a.
20	2.902	n.a.	0.077	n.a.	0.042	n.a.
30	1.966	n.a.	n.a.	n.a.	0.067	n.a.
40	1.484	n.a.	0.017	n.a.	0.067	n.a.
50	0.473	0.0298	8.76	n.a.	0.135	n.a.
60	0.317	n.a.	5.733	n.a.	0.046	n.a.
90	0.157	n.a.	4.01	n.a.	n.a.	n.a.
120	0.059	n.a.	2.363	n.a.	0.087	n.a.
150	0.111	0.0118	0.862	0.039	8.885	n.a.
180	0.129	n.a.	0.516	0.0092	3.208	n.a.
210	0.094	n.a.	0.174	n.a.	2.853	n.a.
240	0.077	n.a.	0.042	n.a.	1.927	n.a.
280	n.a.	n.a.	0.067	n.a.	1.823	n.a.
330	0.017	n.a.	0.067	n.a.	0.728	0.0365

Table B-6. Reaction kinetic data for electrochemical reduction of RDX, experiment #6.

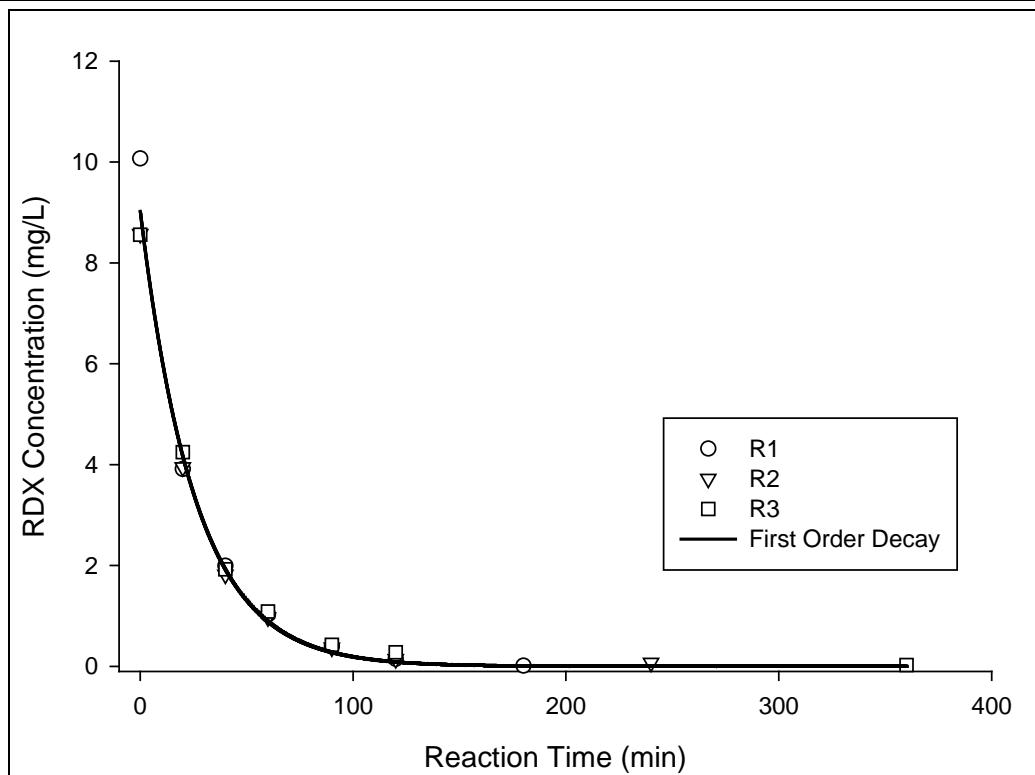
Experimental Run : 6		1 st Order Reaction Coefficient, $k = 0.035 \text{ min}^{-1}$	
Electrode width =	8.00 cm	Standard Deviation of $k = 0.001 \text{ min}^{-1}$	
Submerged depth =	7.62 cm	95% Confidence Interval Of $k = 0.003 \text{ min}^{-1}$	
Cathode Area =	300.11 cm ²	Mass Transfer Based Reaction Coefficient, $k_m = 0.00058 \text{ m/min}$	
Current =	150 mA	95% Confidence Interval Of $k_m = 0.00006 \text{ m/min}$	
Current Density =	5.0 A/m ²		



Reaction Time (min)	Reactor 1		Reactor 2		Reactor 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	8.094	n.a.	8.674	n.a.	8.746	n.a.
20	3.689	n.a.	3.77	n.a.	3.938	n.a.
40	1.476	n.a.	2.219	n.a.	2.019	n.a.
60	1.234	n.a.	1.695	n.a.	1.842	n.a.
90	1.152	n.a.	0.608	n.a.	0.508	n.a.
120	0.473	n.a.	0.575	n.a.	0.727	0.078
180	0.26	n.a.	0.238	n.a.	0.335	n.a.
240	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
360	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Table B- 7. Reaction kinetic data for electrochemical reduction of RDX, experiment #7.

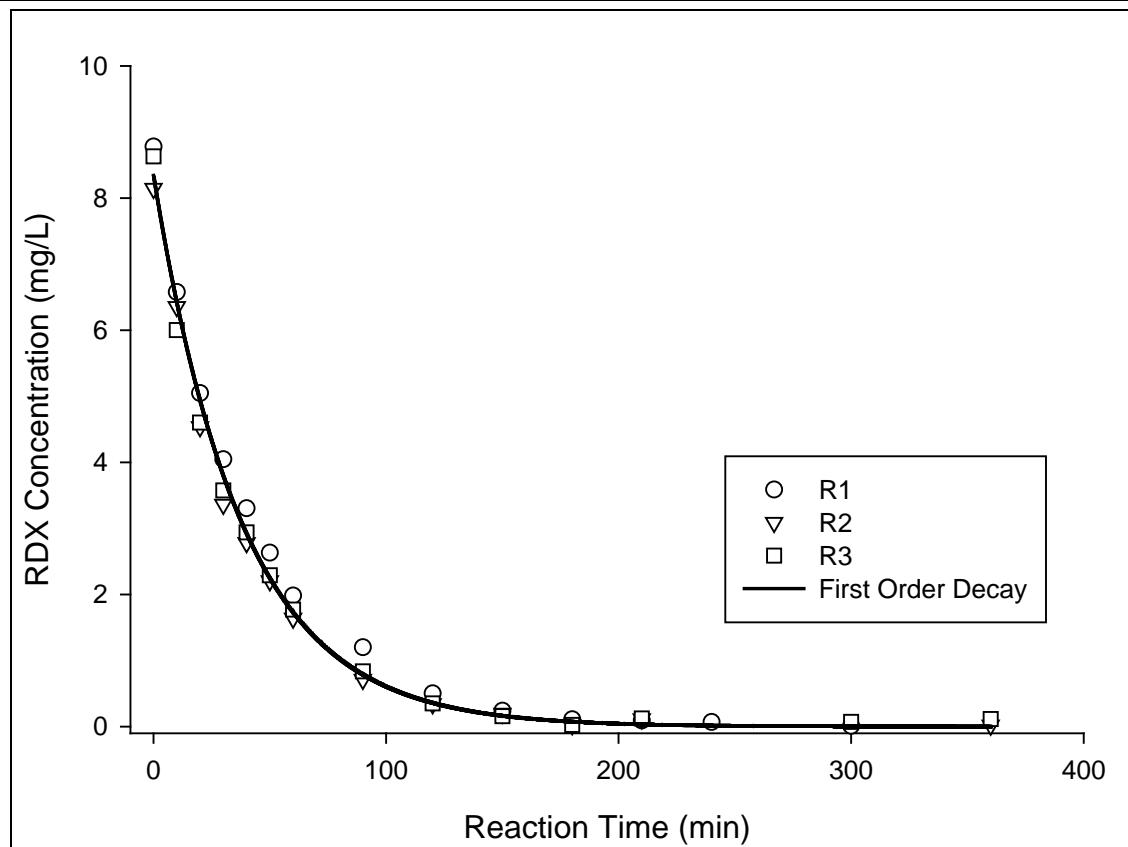
Experimental Run : 7		1 st Order Reaction Coefficient, k = 0.039 min ⁻¹	
Electrode width =	8.00 cm	Standard Deviation of k =	0.002 min ⁻¹
Submerged depth =	7.62 cm	95% Confidence Interval Of k =	0.004 min ⁻¹
Cathode Area =	300.11 cm ²	Mass Transfer Based Reaction Coefficient, k _m =	0.00064 m/min
Current =	125 mA	95% Confidence Interval Of k _m =	0.00006 m/min
Current Density =	4.2 A/m ²		



Reaction Time (min)	Reactor 1		Reactor 2		Reactor 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	10.069	n.a.	8.572	n.a.	8.559	n.a.
20	3.912	n.a.	3.946	n.a.	4.247	0.1005
40	1.994	0.1065	1.818	0.0902	1.923	0.1139
60	1.027	0.1186	0.971	0.0466	1.086	0.0477
90	0.394	0.0383	0.373	n.a.	0.427	0.0373
120	0.146	n.a.	0.145	0.0092	0.278	n.a.
180	0.011	n.a.	n.a.	n.a.	n.a.	n.a.
240	n.a.	n.a.	0.072	n.a.	n.a.	n.a.
360	n.a.	n.a.	n.a.	n.a.	0.025	n.a.

Table B-8. Reaction kinetic data for electrochemical reduction of RDX, experiment #8.

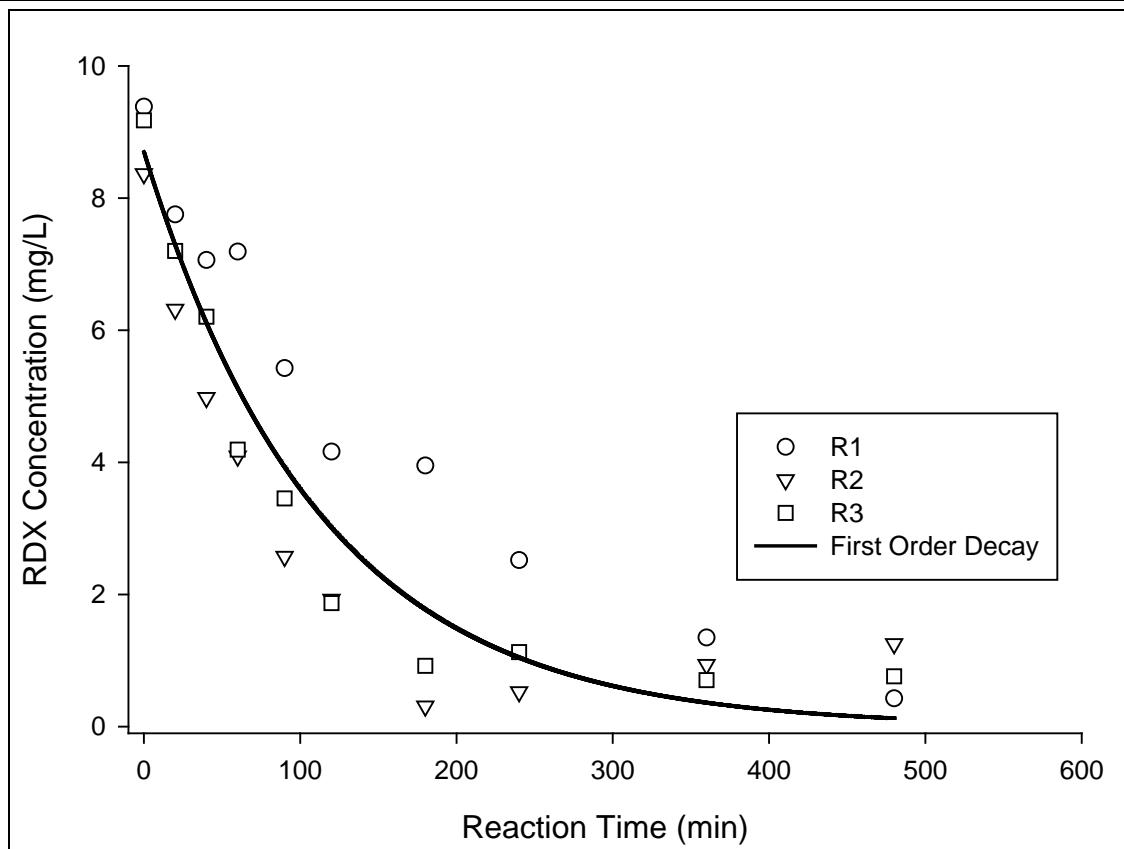
Experimental Run : 8		1 st Order Reaction Coefficient, $k = 0.0262 \text{ min}^{-1}$	
Electrode width =	8.00 cm	Standard Deviation of $k = 0.0006 \text{ min}^{-1}$	
Submerged depth =	7.62 cm	95% Confidence Interval Of $k = 0.0014 \text{ min}^{-1}$	
Cathode Area =	300.11 cm ²	Mass Transfer Based Reaction Coefficient, $k_m = 0.00044 \text{ m/min}$	
Current =	100 mA	95% Confidence Interval Of $k_m = 0.00002 \text{ m/min}$	
Current Density =	3.3 A/m ²		



Reaction Time (min)	Reactor 1		Reactor 2		Reactor 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	8.779	n.a.	8.142	n.a.	8.632	n.a.
10	6.577	n.a.	6.353	n.a.	6.001	n.a.
20	5.046	0.2808	4.537	0.1922	4.601	0.1872
30	4.045	0.3708	3.36	0.2201	3.574	0.2535
40	3.304	0.3791	2.781	0.2282	2.941	0.2524
50	2.631	0.3757	2.203	0.1859	2.29	0.2618
60	1.981	0.3633	1.638	0.1782	1.771	0.236
90	1.199	0.3037	0.713	0.1078	0.837	0.1199
120	0.502	0.1796	0.343	0.0452	0.351	0.0631
150	0.238	0.1217	0.199	0.0182	0.157	0.0176
180	0.11	0.0352	0.026	n.a.	0.025	n.a.
210	0.093	0.0184	0.116	n.a.	0.123	n.a.
240	0.068	n.a.	n.a.	n.a.	n.a.	n.a.
300	0.012	n.a.	n.a.	n.a.	0.073	0.01
360	n.a.	n.a.	0.021	n.a.	0.114	n.a.

Table B-9. Reaction kinetic data for electrochemical reduction of RDX, experiment #9.

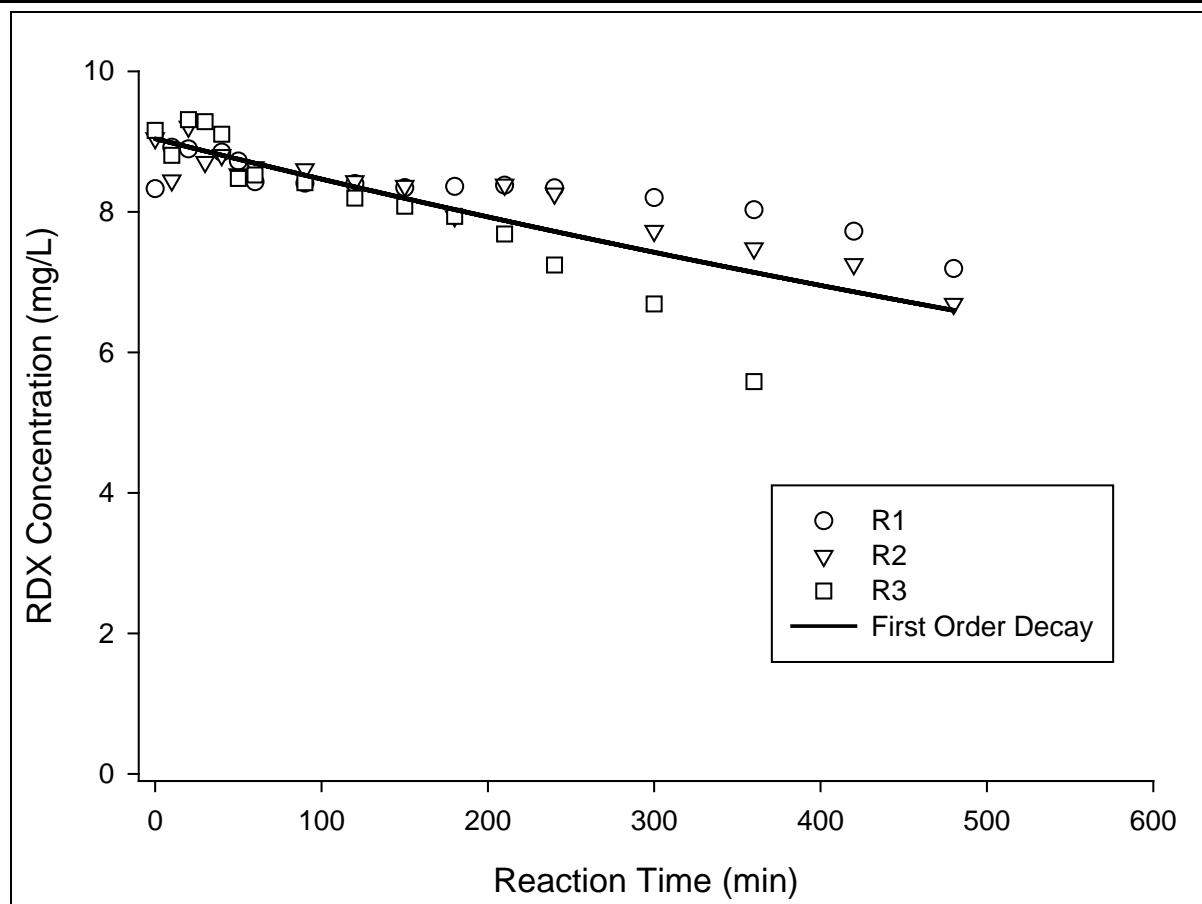
Experimental Run : 9	
Electrode width =	8.00 cm
Submerged depth =	7.62 cm
Cathode Area =	300.11 cm ²
Current =	75 mA
Current Density =	2.5 A/m ²
1 st Order Reaction Coefficient, k =	0.009 min ⁻¹
Standard Deviation of k =	0.001 min ⁻¹
95% Confidence Interval Of k =	0.002 min ⁻¹
Mass Transfer Based Reaction Coefficient, k _m =	0.00015 m/min
95% Confidence Interval Of k _m =	0.00004 m/min



Reaction Time (min)	Reactor 1		Reactor 2		Reactor 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	9.382	n.a.	8.365	n.a.	9.177	n.a.
20	7.75	n.a.	6.314	n.a.	7.198	n.a.
40	7.062	n.a.	4.977	0.1053	6.205	0.295
60	7.188	0.5241	4.091	n.a.	4.193	0.2903
90	5.424	0.8713	2.575	0.1899	3.453	0.3817
120	4.162	0.6329	1.923	n.a.	1.87	n.a.
180	3.95	0.7394	0.309	n.a.	0.92	n.a.
240	2.52	0.6923	0.524	n.a.	1.129	n.a.
360	1.348	0.3443	0.936	n.a.	0.703	n.a.
480	0.428	n.a.	1.253	n.a.	0.761	n.a.

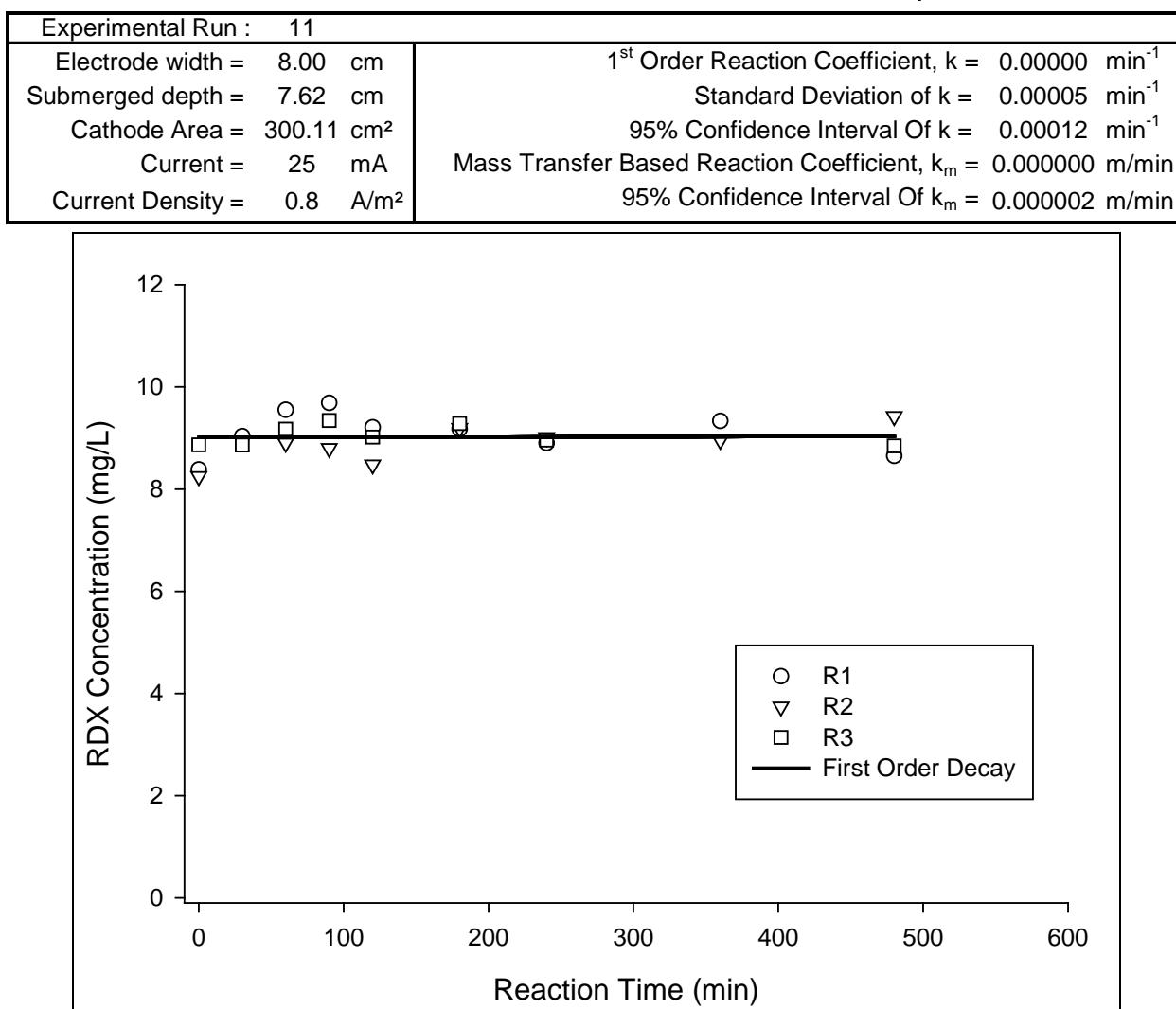
Table B- 10. Reaction kinetic data for electrochemical reduction of RDX, experiment #10.

Experimental Run : 10		1 st Order Reaction Coefficient, $k = 0.00070 \text{ min}^{-1}$
Electrode width =	8.00 cm	Standard Deviation of $k = 0.00008 \text{ min}^{-1}$
Submerged depth =	7.62 cm	95% Confidence Interval Of $k = 0.00018 \text{ min}^{-1}$
Cathode Area =	300.11 cm ²	Mass Transfer Based Reaction Coefficient, $k_m = 0.000012 \text{ m/min}$
Current =	50 mA	95% Confidence Interval Of $k_m = 0.000003 \text{ m/min}$
Current Density =	1.7 A/m ²	



Reaction Time (min)	Reactor 1		Reactor 2		Reactor 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	8.327	n.a.	8.36	0.035	8.708	n.a.
10	8.917	0.1236	8.377	0.0525	8.807	n.a.
20	8.892	n.a.	8.339	0.0636	8.534	0.0215
30	0	n.a.	8.201	0.0775	8.634	0.0505
40	8.847	n.a.	8.029	0.2164	8.604	0.0454
50	8.72	0.0218	7.721	0.298	8.434	0.0456
60	8.426	n.a.	7.191	0.4022	8.369	0.0552
90	8.407	0.0317	9.046	n.a.	7.934	0.0877
120	8.399	0.0248	8.447	n.a.	8.384	0.0848
150	8.343	0.0435	9.212	n.a.	8.258	0.0853

Table B- 11. Reaction kinetic data for electrochemical reduction of RDX, experiment #11.

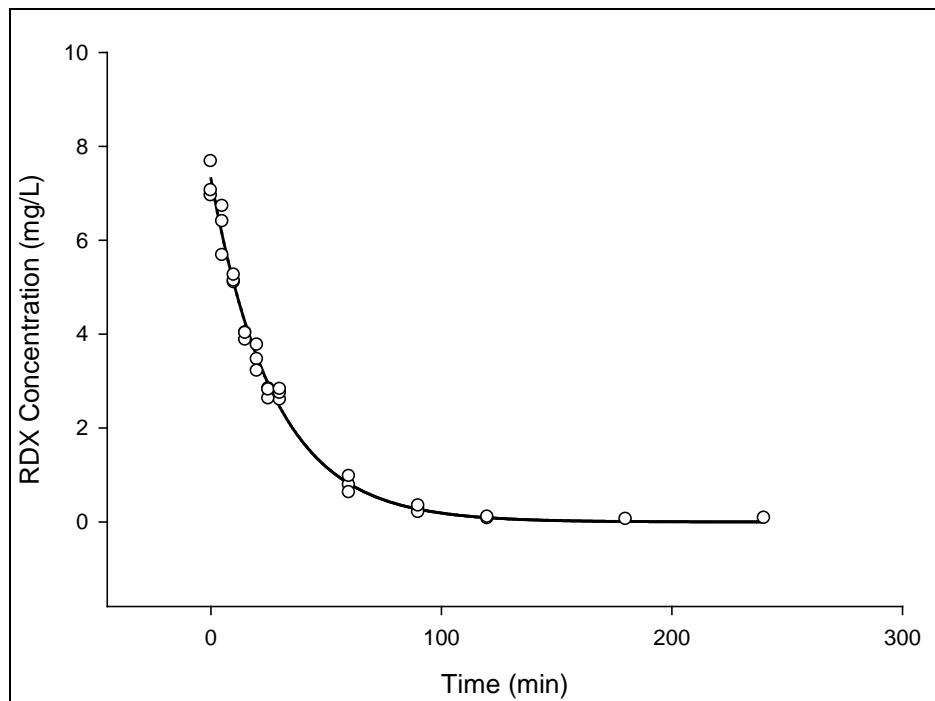


Reaction Time (min)	Reactor 1		Reactor 2		Reactor 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	8.382	0.1174	8.246	n.a.	8.867	n.a.
30	9.034	n.a.	8.901	n.a.	8.861	n.a.
60	9.551	n.a.	8.796	n.a.	9.174	n.a.
90	9.684	n.a.	8.476	n.a.	9.342	0.0859
120	9.208	n.a.	9.192	n.a.	9.017	n.a.
180	9.176	n.a.	9.011	n.a.	9.283	n.a.
240	8.9	n.a.	8.955	n.a.	8.958	n.a.
360	9.333	n.a.	9.423	n.a.	0	0.1729
480	8.65	n.a.	8.867	n.a.	8.846	n.a.

Appendix C. Supporting Data for Electrochemical Bench Pilot Batch Reactor

Table C-1. . Reaction kinetic data for rotating electrode batch reactor, experiment #1.

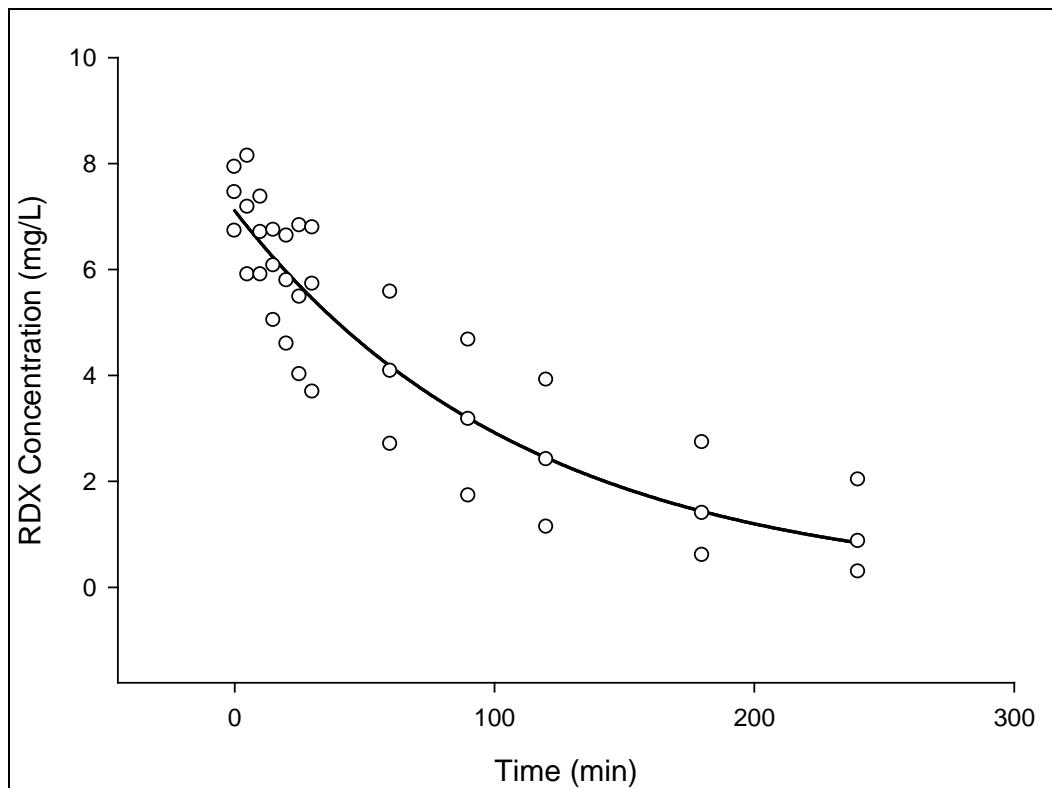
Run: 1		Plate Configuration	
Current =	800 mA	1 st Order Reaction Coefficient, k =	0.037 min ⁻¹
Current Density =	11.2 A/m ²	95% Confidence Interval of k =	0.003 min ⁻¹
Electrode Spacing =	2 mm	Mass Transfer Based Reaction Coefficient, k _m =	0.0014 m/min
		95% Confidence Interval of k _m =	0.0001 m/min



Reaction Time (min)	Reaction Run 1		Reaction Run 2		Reaction Run 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	7.678	0.7013	6.949	n.a.	7.063	n.a.
5	6.723	0.7304	5.679	n.a.	6.4	n.a.
10	5.102	0.8337	5.134	n.a.	5.261	0.142
15	4.03	0.7606	3.875	n.a.	4.021	n.a.
20	3.463	0.7672	3.214	n.a.	3.772	0.0968
25	2.837	0.7969	2.628	n.a.	2.816	0.1874
30	2.604	0.2094	2.746	0.1198	2.827	0.1806
60	0.785	0.1017	0.628	0.0621	0.974	0.0979
90	0.27	0.0339	0.208	0.02	0.347	0.0596
120	0.073	n.a.	n.a.	n.a.	0.105	0.0314
180	n.a.	n.a.	0.059	n.a.	n.a.	n.a.
240	n.a.	n.a.	0.083	n.a.	n.a.	n.a.

Table C- 2. Reaction kinetic data for rotating electrode batch reactor, experiment #2.

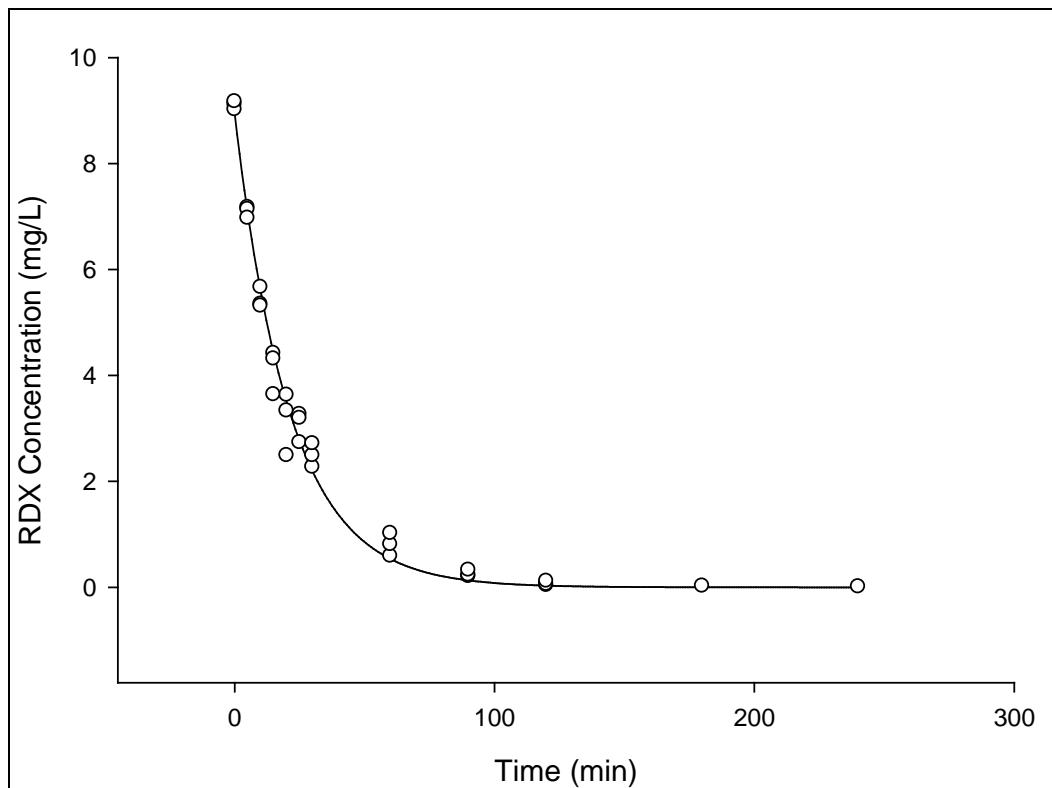
Run: 2		Plate Configuration	
Current =	800 mA	1 st Order Reaction Coefficient, k =	0.009 min ⁻¹
Current Density =	11.2 A/m ²	95% Confidence Interval of k =	0.001 min ⁻¹
Electrode Spacing =	8 mm	Mass Transfer Based Reaction Coefficient, k _m =	0.0003 m/min
		95% Confidence Interval of k _m =	0.0001 m/min



Reaction Time (min)	Reaction Run 1		Reaction Run 2		Reaction Run 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	6.725	n.a.	7.454	n.a.	7.932	n.a.
5	5.902	n.a.	7.175	n.a.	8.141	0.0911
10	5.903	n.a.	6.7	n.a.	7.37	n.a.
15	5.038	n.a.	6.072	n.a.	6.743	n.a.
20	4.593	n.a.	5.792	n.a.	6.632	n.a.
25	4.018	n.a.	5.48	0.1365	6.829	n.a.
30	3.686	n.a.	5.725	0.1154	6.79	0.1517
60	2.704	n.a.	4.083	0.1278	5.576	0.2132
90	1.729	n.a.	3.171	0.1562	4.668	0.2246
120	1.137	n.a.	2.412	0.1779	3.912	0.2505
180	0.604	n.a.	1.399	0.1735	2.732	0.2679
240	0.292	n.a.	0.869	0.108	2.028	0.2192

Table C- 3. Reaction kinetic data for rotating electrode batch reactor, experiment #3.

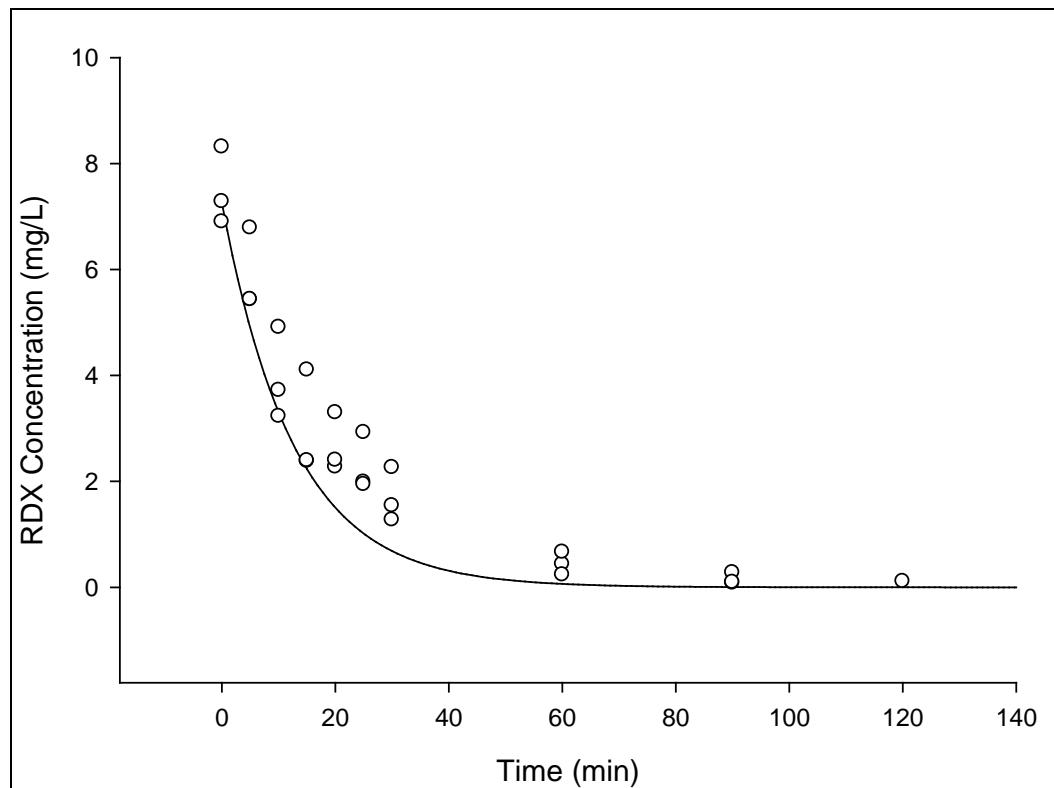
Run: 3		Plate Configuration	
Current =	800 mA	1 st Order Reaction Coefficient, k =	0.047 min ⁻¹
Current Density =	11.2 A/m ²	95% Confidence Interval of k =	0.002 min ⁻¹
Electrode Spacing =	4 mm	Mass Transfer Based Reaction Coefficient, k _m =	0.0018 m/min
		95% Confidence Interval of k _m =	0.0001 m/min



Reaction Time (min)	Reaction Run 1		Reaction Run 2		Reaction Run 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	9.119	n.a.	9.021	0.7619	9.168	0.3253
5	7.174	n.a.	7.135	0.7143	6.97	0.3203
10	5.345	n.a.	5.313	0.5759	5.666	0.5011
15	4.417	0.7288	4.315	0.5308	3.64	0.5921
20	2.491	0.7443	3.63	0.4963	3.334	0.1589
25	2.732	0.7144	3.267	0.6402	3.193	0.3713
30	2.271	0.1155	2.487	0.1978	2.713	0.1591
60	0.588	0.1277	0.808	0.1402	1.021	0.0646
90	0.204	0.0964	0.231	0.1136	0.325	0.0554
120	0.037	0.067	0.058	0.0096	0.115	n.a.
180	n.a.	0.0618	n.a.	0.0713	0.026	n.a.
240	n.a.	0.063	n.a.	0.0771	0.012	n.a.

Table C- 4. Reaction kinetic data for rotating electrode batch reactor, experiment #4.

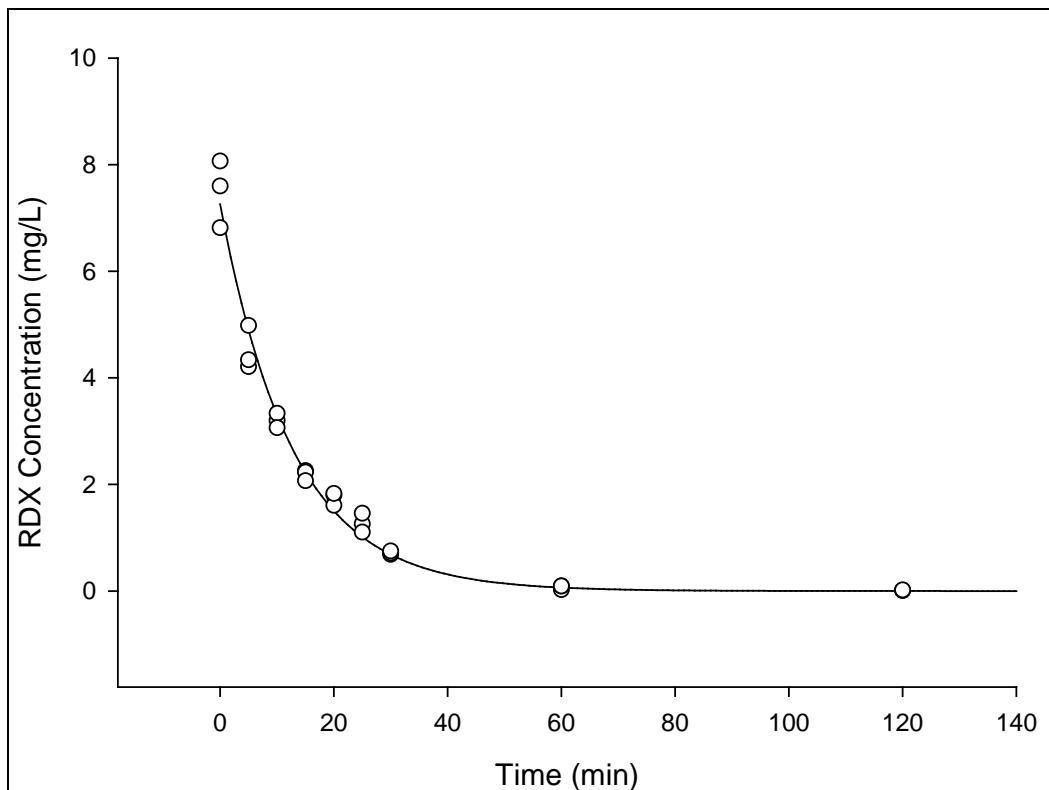
Run: 4 Cross Configuration		1 st Order Reaction Coefficient, k = 0.053 min ⁻¹	
Current = 1000 mA	Current Density = 8.1 A/m ²	95% Confidence Interval of k = 0.009 min ⁻¹	
		Mass Transfer Based Reaction Coefficient, k _m = 0.0012 m/min	95% Confidence Interval of k _m = 0.0002 m/min



Reaction Time (min)	Reaction Run 1		Reaction Run 2		Reaction Run 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	8.315	0.5366	6.899	n.a.	7.283	n.a.
5	5.432	0.4319	6.787	n.a.	5.438	n.a.
10	3.23	0.5343	4.912	n.a.	3.722	0.2786
15	2.382	0.7406	4.106	n.a.	2.391	n.a.
20	2.273	0.2027	3.298	0.213	2.404	0.2759
25	1.988	n.a.	2.924	0.0208	1.943	0.2435
30	1.544	0.1203	2.265	0.2913	1.274	0.1915
60	0.438	0.0763	0.666	0.1933	0.239	0.0768
90	0.082	0.0346	0.28	0.0926	0.098	0.0089
120	n.a.	n.a.	0.113	0.0712	n.a.	n.a.
180	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
240	n.a.	n.a.	n.a.	0.005	n.a.	n.a.

Table C- 5. Reaction kinetic data for rotating electrode batch reactor, experiment #5.

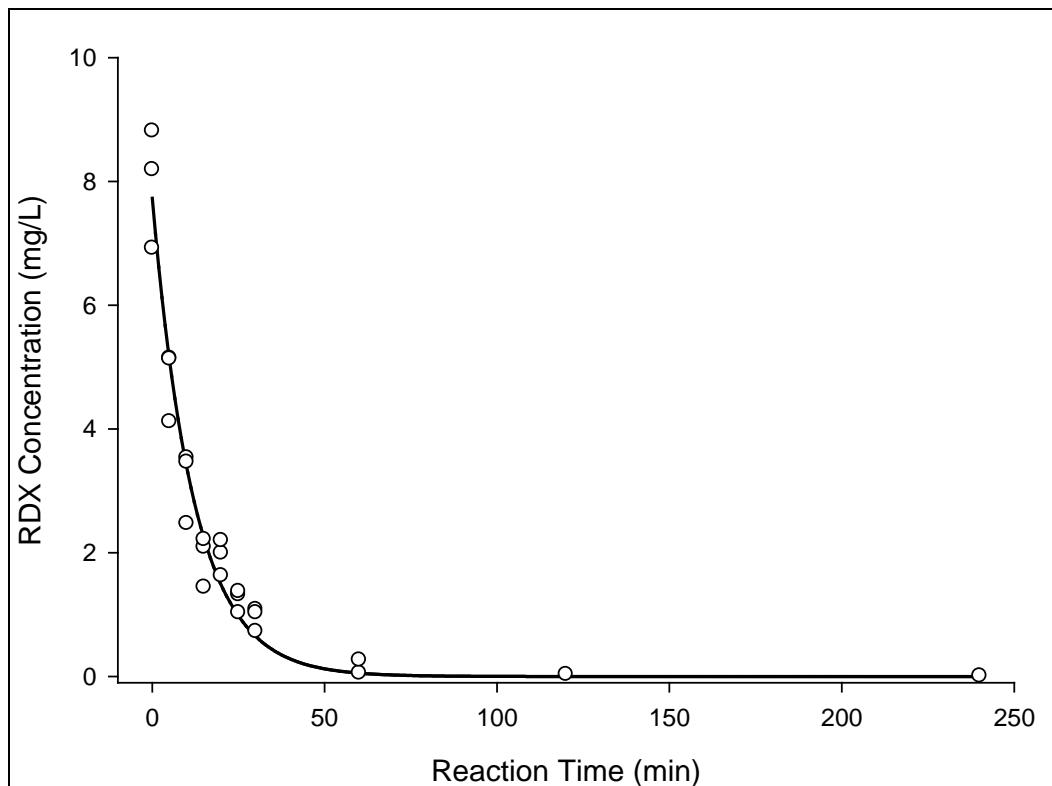
Run: 5 Cross Configuration		1 st Order Reaction Coefficient, k = 0.079 min ⁻¹	
Current = 1500 mA	Current Density = 12.1 A/m ²	95% Confidence Interval of k = 0.007 min ⁻¹	
		Mass Transfer Based Reaction Coefficient, k _m = 0.0017 m/min	95% Confidence Interval of k _m = 0.0002 m/min



Reaction Time (min)	Reaction Run 1		Reaction Run 2		Reaction Run 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	6.816	0.0876	7.597	0.3084	8.065	0.3125
5	4.209	n.a.	4.337	0.4974	4.983	n.a.
10	3.199	n.a.	3.333	0.4713	3.063	0.4833
15	2.259	0.2893	2.231	0.3618	2.07	0.4037
20	1.798	0.0965	1.608	0.1434	1.83	0.1625
25	1.258	0.1309	1.105	0.1204	1.458	0.1532
30	0.686	0.0503	0.715	0.061	0.749	0.0632
60	0.027	n.a.	0.094	0.0062	0.094	0.0169
90	n.a.	n.a.	n.a.	0.0054	n.a.	n.a.
120	0.013	n.a.	0.008	n.a.	0.019	n.a.
180	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
240	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Table C- 6. Reaction kinetic data for rotating electrode batch reactor, experiment #6.

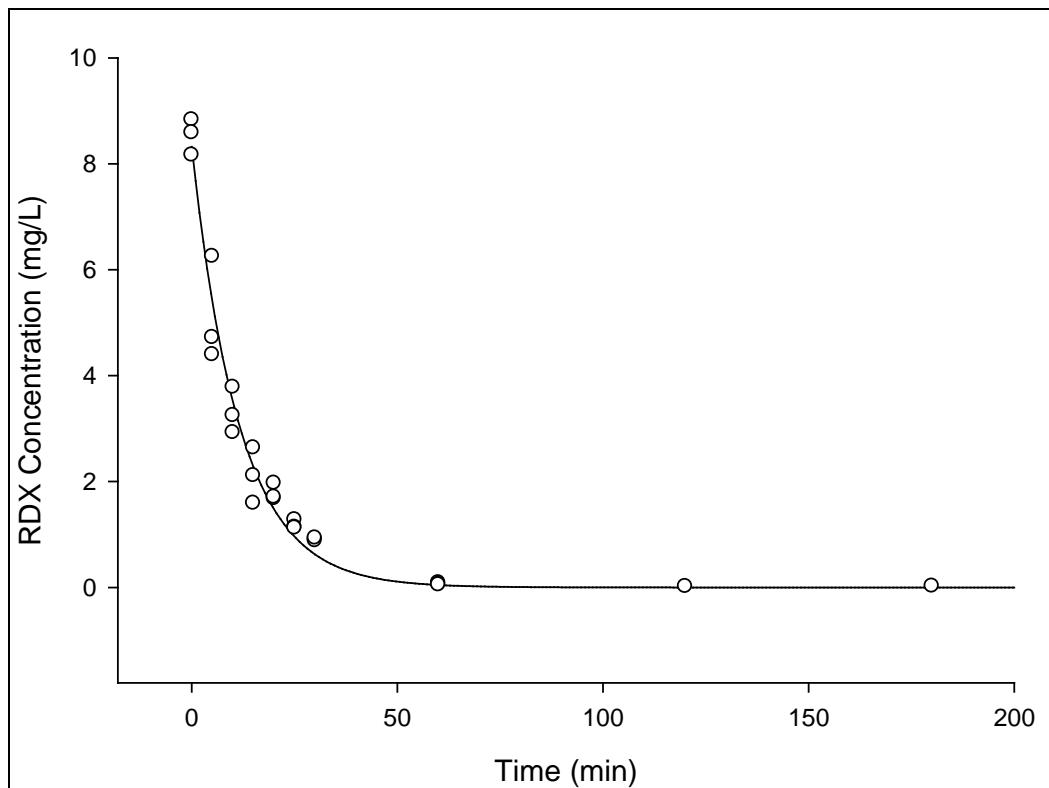
Run: 6 Cross Configuration		1 st Order Reaction Coefficient, k = 0.083 min ⁻¹	
Current = 2000 mA	Current Density = 16.2 A/m ²	95% Confidence Interval of k = 0.012 min ⁻¹	
		Mass Transfer Based Reaction Coefficient, k _m = 0.0018 m/min	95% Confidence Interval of k _m = 0.0003 m/min



Reaction Time (min)	Reaction Run 1		Reaction Run 2		Reaction Run 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	6.922	n.a.	8.192	0.1282	8.814	0.242
5	4.117	n.a.	5.144	n.a.	5.134	0.3323
10	2.474	n.a.	3.536	n.a.	3.465	0.1485
15	1.446	n.a.	2.093	n.a.	2.216	n.a.
20	1.631	0.0553	1.996	0.0562	2.199	0.0749
25	1.033	0.0813	1.323	0.0129	1.375	0.0477
30	0.731	0.0177	1.084	0.0143	1.032	0.0289
60	n.a.	0.0335	0.056	n.a.	0.268	n.a.
90	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
120	0.035	n.a.	n.a.	n.a.	n.a.	n.a.
180	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
240	n.a.	n.a.	0.011	0.0087	n.a.	0.0159

Table C- 7. Reaction kinetic data for rotating electrode batch reactor, experiment #7.

Run: 7	Cross Configuration		
Current = 2500 mA	1 st Order Reaction Coefficient, k =	0.086	min ⁻¹
Current Density = 20.2 A/m ²	95% Confidence Interval of k =	0.010	min ⁻¹
	Mass Transfer Based Reaction Coefficient, k _m =	0.0019	m/min
	95% Confidence Interval of k _m =	0.0002	m/min



Appendix D. Supporting Data for Electrochemical Bench Pilot Flow Reactor

Table D- 1. Reactor kinetic data for packed electrode flow reactor.

Current (A)	Current Density (A/m ²)	Flow Rate (L/min)	k _m (m/min)	σ, k _m (m/min)	n	95% CI (m/min)	% Destroyed
1.5	6.96	0.129	0.00074	0.00001	10	0.00003	71.1%
1.75	8.12	0.129	0.00070	0.00002	12	0.00004	69.4%
2	9.28	0.129	0.00061	0.00001	15	0.00002	64.1%
2.5	11.60	0.129	0.00067	0.00003	10	0.00007	67.4%

Table D- 2.. Reactor effluent data for experimental run #1 in the packed electrode flow reactor.

Run #1 December 17, 2007						
C ₀ (mg/L)	A (m ²)	Q (L/min)	C (mg/L)	k _m (m/min)	Current (A)	Voltage (V)
9.059	0.2174	0.129	3.097	0.0006369	2	3.46
9.059	0.2174	0.129	2.752	0.0007070	2	3.46
9.059	0.2174	0.129	3.17	0.0006231	2	3.46
9.059	0.2174	0.129	3.194	0.0006186	2	3.46
9.059	0.2174	0.129	3.195	0.0006184	2	3.46
9.059	0.2174	0.129	3.149	0.0006270	2	3.46
9.059	0.2174	0.129	3.249	0.0006085	2	3.46
9.059	0.2174	0.129	3.226	0.0006127	2	3.46
9.059	0.2174	0.129	3.254	0.0006075	2	3.46
9.059	0.2174	0.129	3.298	0.0005996	2	3.46
9.059	0.2174	0.129	3.235	0.0006110	2	3.46
9.059	0.2174	0.129	3.296	0.0005999	2	3.46
9.059	0.2174	0.129	3.246	0.0006090	2	3.46
9.059	0.2174	0.129	3.274	0.0006039	2	3.46
9.059	0.2174	0.129	3.274	0.0006039	2	3.46
9.059	0.2174	0.129	3.334	0.0005931	2	3.46
9.059	0.2174	0.129	3.327	0.0005944	2	3.46
9.059	0.2174	0.129	3.002	0.0006554	2	3.46
9.059	0.2174	0.129	3.162	0.0006246	2.5	3.69
9.059	0.2174	0.129	2.882	0.0006796	2.5	3.69
9.059	0.2174	0.129	3.124	0.0006317	2.5	3.69
9.059	0.2174	0.129	2.92	0.0006718	2.5	3.69
9.059	0.2174	0.129	3.066	0.0006429	2.5	3.69
9.059	0.2174	0.129	2.864	0.0006833	2.5	3.69
9.059	0.2174	0.129	2.901	0.0006757	2.5	3.69
9.059	0.2174	0.129	2.792	0.0006984	2.5	3.69
9.059	0.2174	0.129	3.075	0.0006411	2.5	3.69
9.059	0.2174	0.129	2.789	0.0006990	2.5	3.69
9.059	0.2174	0.129	3.089	0.0006384	2.5	3.69

Table D- 3. Reactor effluent data for experimental run #2 in the packed electrode flow reactor.

Run #2 December 18, 2007						
C ₀ (mg/L)	A (m ²)	Q (L/min)	C (mg/L)	k _m (m/min)	Current (A)	Voltage (V)
5.395	0.2174	0.129	1.685	0.0006905	1.5	3
5.395	0.2174	0.129	1.665	0.0006976	1.5	3
5.395	0.2174	0.129	1.706	0.0006832	1.5	3
5.395	0.2174	0.129	1.596	0.0007227	1.5	3
5.395	0.2174	0.129	1.661	0.0006990	1.5	3
5.395	0.2174	0.129	1.56	0.0007363	1.5	3
5.395	0.2174	0.129	1.57	0.0007325	1.5	3
5.395	0.2174	0.129	1.59	0.0007250	1.5	3
5.395	0.2174	0.129	1.598	0.0007220	1.5	3
5.395	0.2174	0.129	1.506	0.0007572	1.5	3
5.395	0.2174	0.129	1.594	0.0007235	1.5	3
5.395	0.2174	0.129	1.513	0.0007544	1.5	3
5.395	0.2174	0.129	1.548	0.0007408	1.5	3
5.395	0.2174	0.129	1.539	0.0007443	1.5	3
5.395	0.2174	0.129	1.57	0.0007325	1.5	3
4.384	0.2174	0.129	1.415	0.0006710	1.75	3.3
4.384	0.2174	0.129	1.339	0.0007038	1.75	3.3
4.384	0.2174	0.129	1.404	0.0006756	1.75	3.3
4.384	0.2174	0.129	1.336	0.0007051	1.75	3.3
4.384	0.2174	0.129	1.396	0.0006790	1.75	3.3
4.384	0.2174	0.129	1.381	0.0006854	1.75	3.3
4.384	0.2174	0.129	1.368	0.0006911	1.75	3.3
4.384	0.2174	0.129	1.254	0.0007427	1.75	3.3
4.384	0.2174	0.129	1.371	0.0006898	1.75	3.3
4.384	0.2174	0.129	1.352	0.0006980	1.75	3.3
4.384	0.2174	0.129	1.334	0.0007060	1.75	3.3
4.384	0.2174	0.129	1.341	0.0007029	1.75	3.3
4.384	0.2174	0.129	1.34	0.0007033	1.75	3.3
4.384	0.2174	0.129	1.299	0.0007218	1.75	3.3
4.384	0.2174	0.129	1.337	0.0007047	1.75	3.3

Appendix E. Supporting Data for Alkaline Assisted Electrochemical Reactor

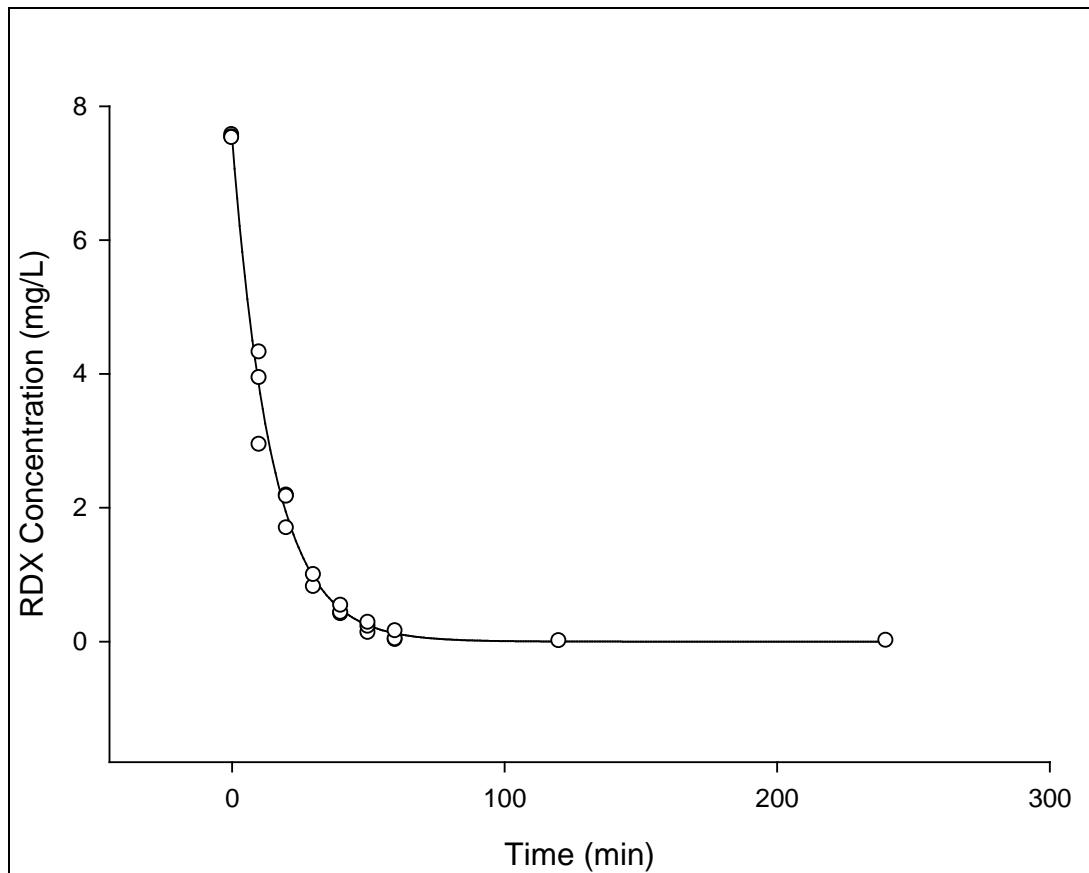
Table E- 1. Reaction kinetic data for the alkaline assisted electrochemical reduction of RDX, experiment #1.

Run: 1		Small Batch Reactors		1 st Order Reaction Coefficient, k = 0.00020 min ⁻¹	
Hydroxide, [OH ₋] =	0.5 mM			95% Confidence Interval of k = 0.00002 min ⁻¹	
Current Density =	0 A/m ²			Mass Transfer Based Reaction Coefficient, k _m = 0.0000033 m/min	
				95% Confidence Interval of k _m = 0.0000004 m/min	

Reaction Time (hr)	Reaction Run 1		Reaction Run 2		Reaction Run 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	0.988	0.0676	0.063	n.a.	1.397	n.a.
2	0.901	n.a.	0.874	n.a.	1.101	0.3386
4	0.831	n.a.	0.836	n.a.	0.8	n.a.
24	0.716	n.a.	0.731	n.a.	0.742	n.a.
48	0.516	n.a.	0.519	n.a.	0.598	n.a.
72	0.444	n.a.	0.403	n.a.	0.46	n.a.
96	0.415	n.a.	0.362	n.a.	0.403	n.a.
120	0.332	n.a.	0.339	n.a.	0.34	n.a.
144	0.25	n.a.	0.274	n.a.	0.278	n.a.
168	0.191	n.a.	0.237	n.a.	0.34	0.1942
192	0.216	n.a.	0.234	n.a.	0.179	n.a.
216	0.08	n.a.	0.096	n.a.	0.166	n.a.
240	0.081	n.a.	0.154	n.a.	0.18	n.a.
264	0.049	n.a.	0.161	n.a.	0.124	n.a.
288	0.026	n.a.	0.08	n.a.	0.038	n.a.
312	0.042	n.a.	n.a.	n.a.	0.065	n.a.
336	0.014	n.a.	0.051	n.a.	0.014	n.a.

Table E- 2. Reaction kinetic data for the alkaline assisted electrochemical reduction of RDX, experiment #2.

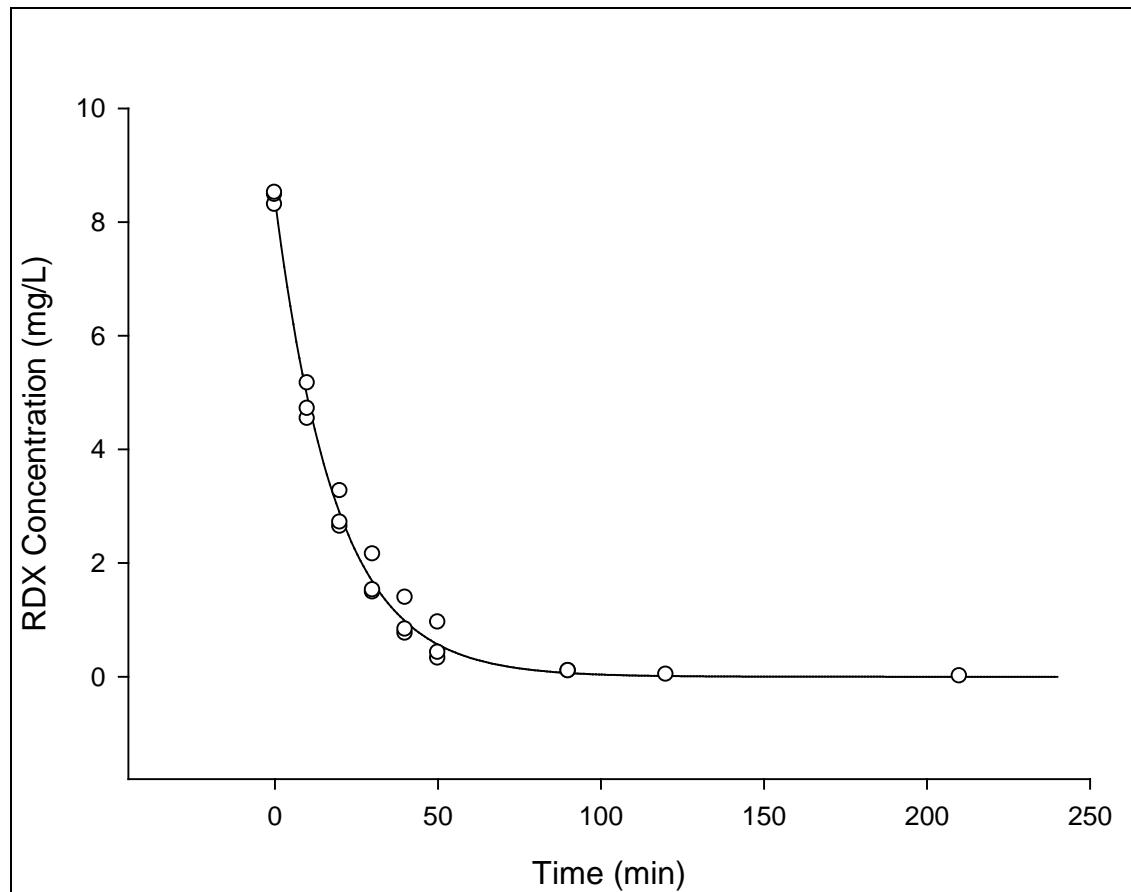
Run: 2		Small Batch Reactors	
Hydroxide, $[\text{OH}_-]$ =	100 mM	1 st Order Reaction Coefficient, k =	0.0688 min^{-1}
Current Density =	4.3 A/m ²	95% Confidence Interval of k =	0.0060 min^{-1}
		Mass Transfer Based Reaction Coefficient, k_m =	0.0011 m/min
		95% Confidence Interval of k_m =	0.0001 m/min



Reaction Time (min)	Reaction Run 1		Reaction Run 2		Reaction Run 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	7.57	n.a.	7.536	n.a.	7.526	n.a.
10	2.941	n.a.	4.322	n.a.	3.938	n.a.
20	2.183	n.a.	1.694	n.a.	2.166	n.a.
30	1.1315	n.a.	0.817	n.a.	0.997	n.a.
40	0.409	n.a.	0.431	n.a.	0.537	n.a.
50	0.132	n.a.	0.224	n.a.	0.281	n.a.
60	0.024	n.a.	0.035	n.a.	0.155	n.a.
90	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
120	0.007	n.a.	n.a.	n.a.	n.a.	n.a.
150	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
180	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
210	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
240	n.a.	n.a.	n.a.	n.a.	0.013	n.a.

Table E- 3. Reaction kinetic data for the alkaline assisted electrochemical reduction of RDX, experiment #3.

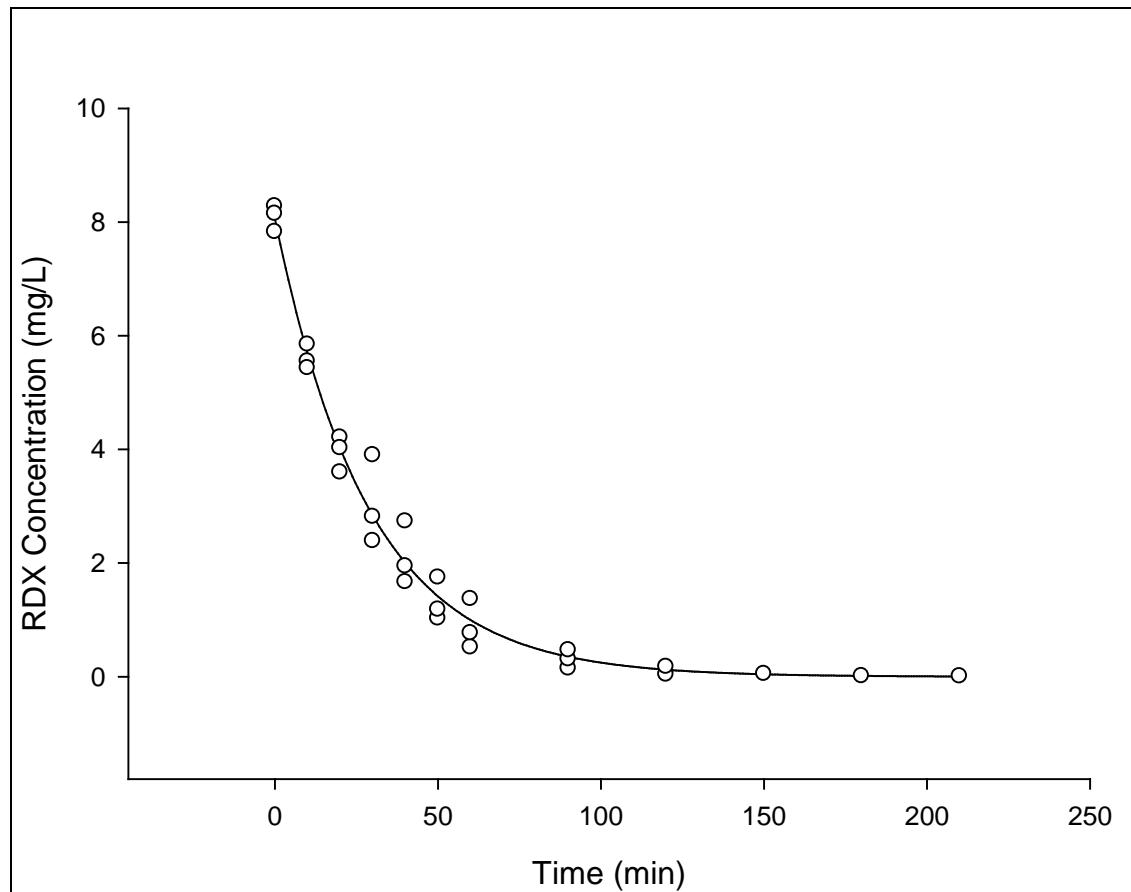
Run: 3		Small Batch Reactors	
Hydroxide, $[\text{OH}_-]$ =	0.5 mM	1 st Order Reaction Coefficient, k =	0.0539 min^{-1}
Current Density =	4.3 A/m ²	95% Confidence Interval of k =	0.0038 min^{-1}
		Mass Transfer Based Reaction Coefficient, k_m =	0.0009 m/min
		95% Confidence Interval of k_m =	0.0001 m/min



Reaction Time (min)	Reaction Run 1		Reaction Run 2		Reaction Run 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	8.307	n.a.	8.48	n.a.	8.514	n.a.
10	4.536	n.a.	4.716	n.a.	5.163	n.a.
20	2.638	0.0435	2.714	0.0518	3.265	0.0339
30	1.483	0.0228	1.521	0.0132	2.154	0.0378
40	0.761	n.a.	0.832	0.0293	1.39	n.a.
50	0.324	n.a.	0.422	n.a.	0.956	n.a.
90	0.101	n.a.	n.a.	n.a.	0.101	n.a.
120	n.a.	n.a.	n.a.	n.a.	0.037	n.a.
150	n.a.	n.a.	n.a.	0.0043	n.a.	n.a.
180	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
210	n.a.	n.a.	n.a.	n.a.	0.008	n.a.
240	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Table E- 4. Reaction kinetic data for the alkaline assisted electrochemical reduction of RDX, experiment #4.

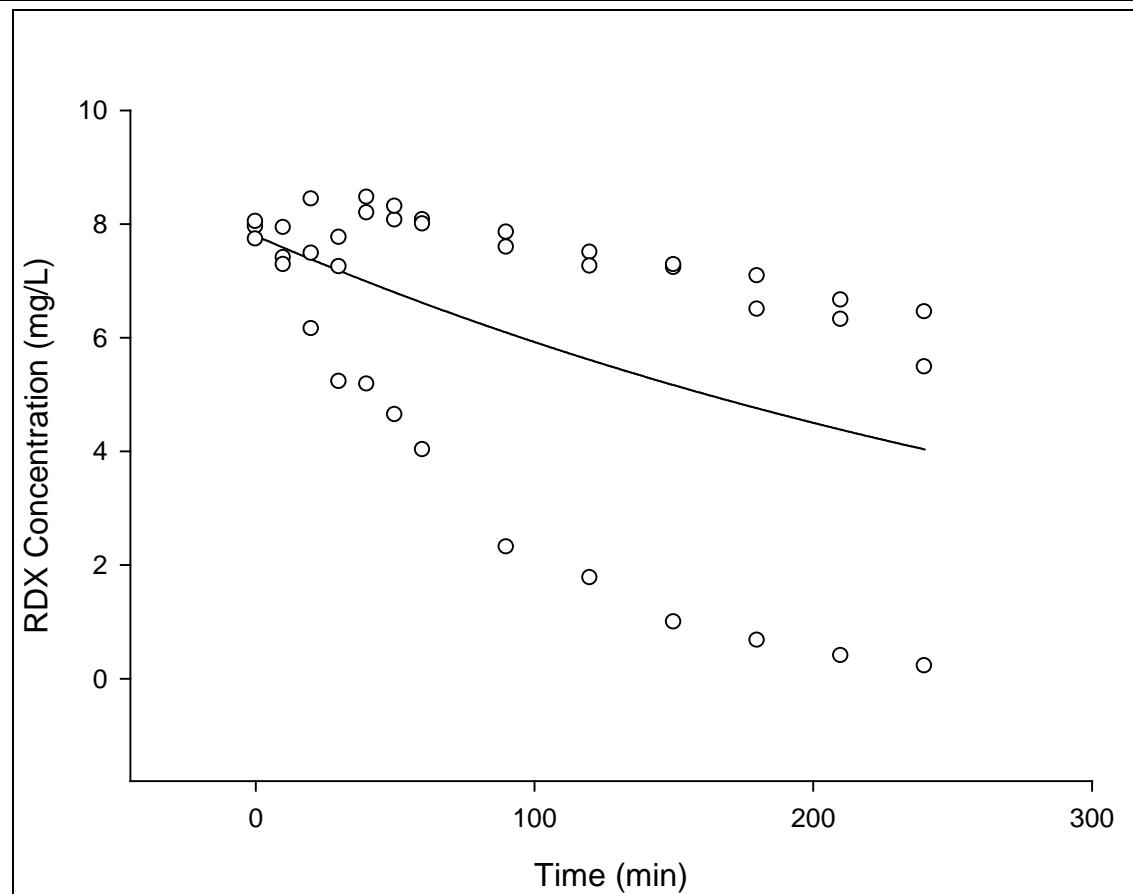
Run: 4		Small Batch Reactors	
Hydroxide, $[\text{OH}_-]$	= 0.0001 mM	1 st Order Reaction Coefficient, k =	0.0348 min^{-1}
Current Density	= 4.3 A/m ²	95% Confidence Interval of k =	0.0033 min^{-1}
		Mass Transfer Based Reaction Coefficient, k_m =	0.0006 m/min
		95% Confidence Interval of k_m =	0.0001 m/min



Reaction Time (min)	Reaction Run 1		Reaction Run 2		Reaction Run 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	8.28	n.a.	7.828	n.a.	8.146	n.a.
10	5.845	n.a.	5.549	n.a.	5.431	n.a.
20	3.596	0.0927	4.211	n.a.	4.024	n.a.
30	2.389	0.0274	2.815	0.0335	3.9	0.0786
40	1.663	0.0321	1.943	0.067	2.734	0.0853
50	1.025	0.0626	1.181	0.0239	1.744	0.0399
60	0.518	n.a.	0.766	n.a.	1.369	n.a.
90	0.147	n.a.	0.309	n.a.	0.468	n.a.
120	0.04	n.a.	n.a.	n.a.	0.174	n.a.
150	n.a.	n.a.	n.a.	n.a.	0.049	n.a.
180	n.a.	n.a.	n.a.	n.a.	0.012	n.a.
210	n.a.	n.a.	n.a.	n.a.	0.009	n.a.
240	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Table E- 5. Reaction kinetic data for the alkaline assisted electrochemical reduction of RDX, experiment #5.

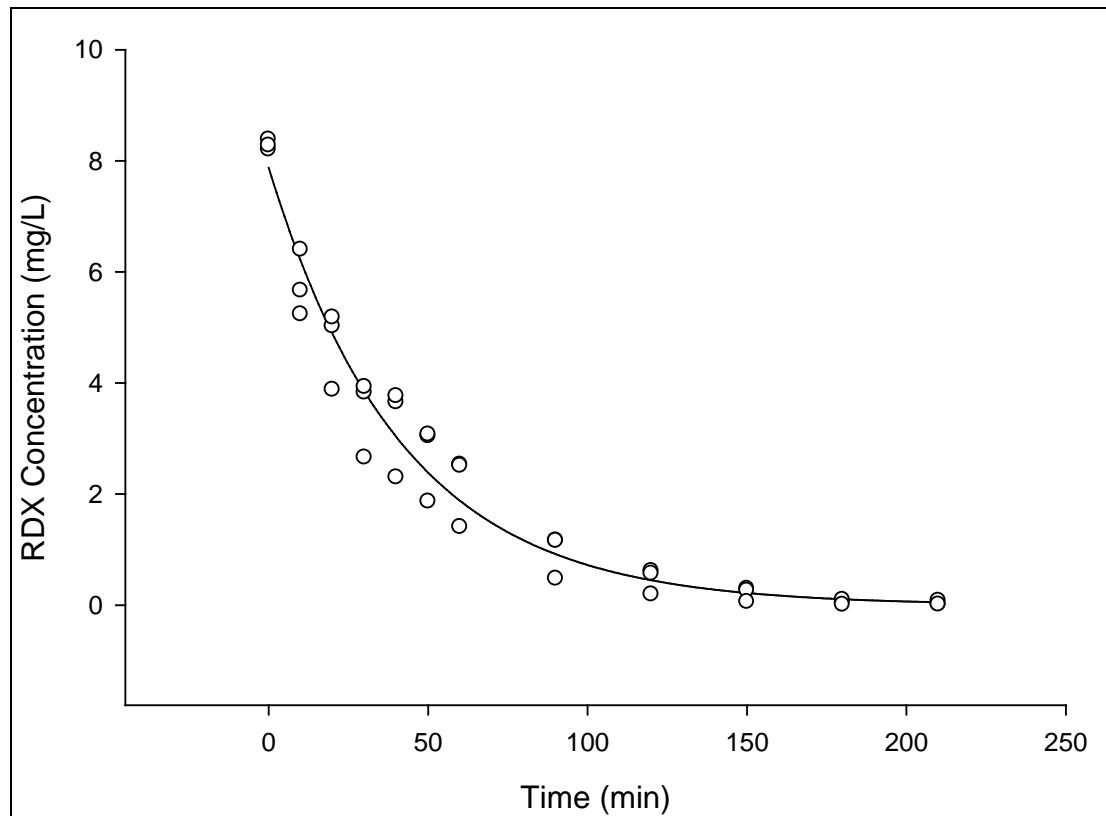
Run: 5		Small Batch Reactors	
Hydroxide, $[\text{OH}_-]$ =	0.5 mM	1 st Order Reaction Coefficient, k =	0.0027 min^{-1}
Current Density =	2.1 A/m^2	95% Confidence Interval of k =	0.0019 min^{-1}
		Mass Transfer Based Reaction Coefficient, k_m =	0.00005 m/min
		95% Confidence Interval of k_m =	0.00003 m/min



Reaction Time (min)	Reaction Run 1		Reaction Run 2		Reaction Run 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	7.948	n.a.	8.038	n.a.	7.731	n.a.
10	7.931	n.a.	7.401	n.a.	7.281	0.1601
20	7.481	n.a.	8.435	n.a.	6.15	n.a.
30	7.759	n.a.	7.245	n.a.	5.224	0.1643
40	8.191	0.0783	8.464	0.087	5.177	0.2332
50	8.063	0.0972	8.306	0.1327	4.641	0.2906
60	8.071	0.1317	7.996	0.1821	4.025	0.316
90	7.587	0.1528	7.852	0.1556	2.311	0.2758
120	7.497	0.1916	7.254	0.2526	1.771	0.2621
150	7.226	0.2506	7.276	0.2846	0.994	0.1964
180	7.082	0.2628	6.495	0.3946	0.67	0.1744
210	6.657	0.3232	6.317	0.4216	0.401	0.1301
240	6.449	0.3543	5.479	0.4936	0.221	0.0877

Table E- 6. Reaction kinetic data for the alkaline assisted electrochemical reduction of RDX, experiment #6.

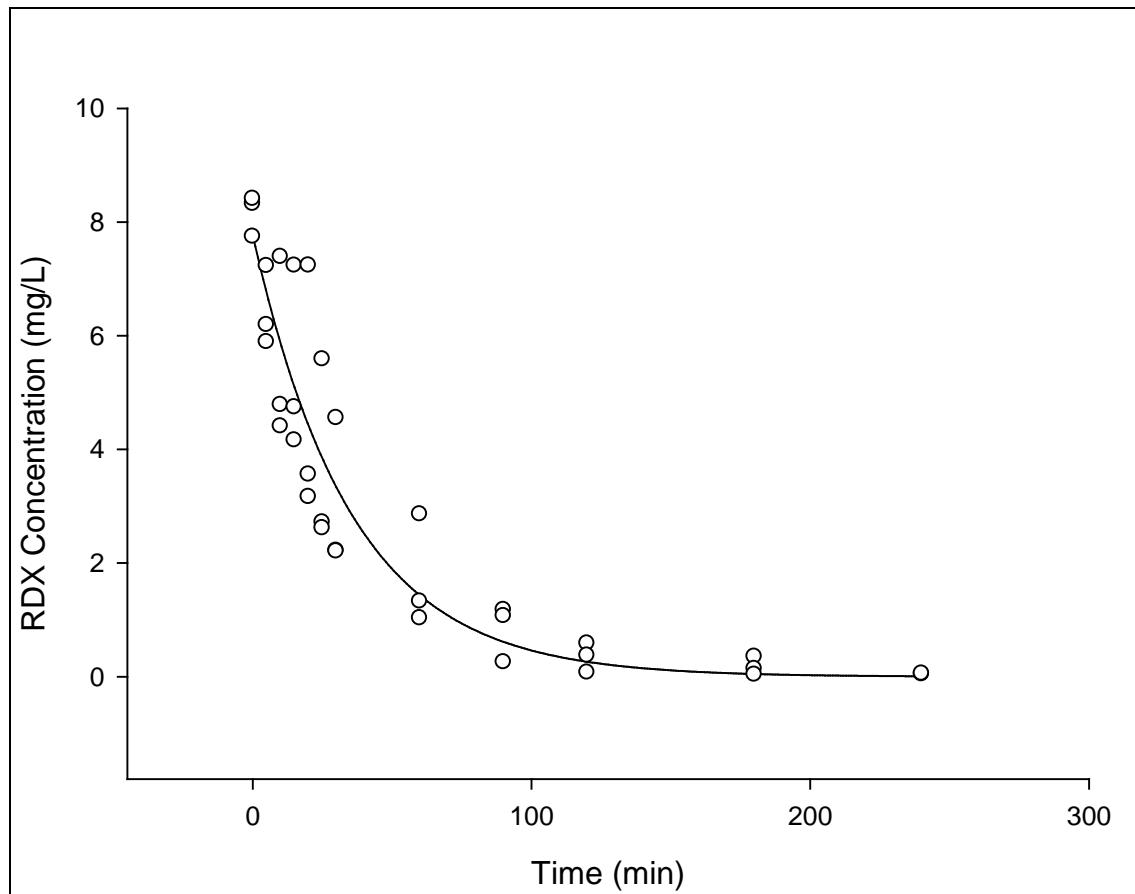
Run: 6		Small Batch Reactors	
Hydroxide, $[\text{OH}_-]$ =	100 mM	1 st Order Reaction Coefficient, k =	0.0239 min^{-1}
Current Density =	2.1 A/m ²	95% Confidence Interval of k =	0.0030 min^{-1}
		Mass Transfer Based Reaction Coefficient, k_m =	0.00040 m/min
		95% Confidence Interval of k_m =	0.00005 m/min



Reaction Time (min)	Reaction Run 1		Reaction Run 2		Reaction Run 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	8.382	n.a.	8.206	n.a.	8.275	n.a.
10	5.664	n.a.	6.402	n.a.	5.237	n.a.
20	5.021	0.0138	5.179	n.a.	3.879	n.a.
30	3.824	n.a.	3.929	n.a.	2.658	0.009
40	3.653	n.a.	3.766	0.005	2.302	n.a.
50	3.043	0.0052	3.074	n.a.	1.867	n.a.
60	2.532	n.a.	2.51	0.0056	1.407	n.a.
90	1.165	n.a.	1.158	n.a.	0.477	n.a.
120	0.617	n.a.	0.569	n.a.	0.195	n.a.
150	0.294	n.a.	0.262	n.a.	0.058	n.a.
180	0.044	n.a.	0.098	n.a.	0.01	n.a.
210	0.02	n.a.	0.079	n.a.	0.012	n.a.
240	n.a.	n.a.	n.a.	0.0059	n.a.	n.a.

Table E- 7. Reaction kinetic data for the alkaline assisted electrochemical reduction of RDX, experiment #7.

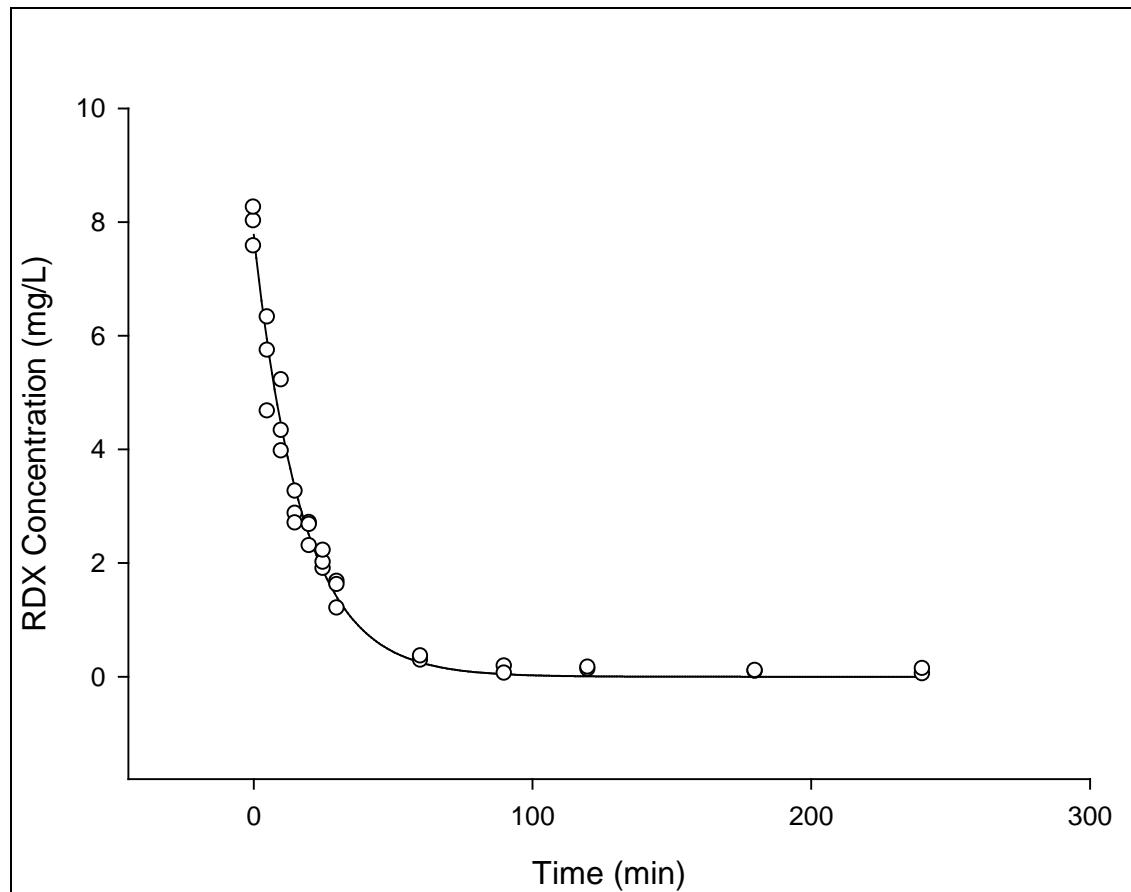
Run: 7 Benchtop Pilot Reactor		1 st Order Reaction Coefficient, k = 0.028 min ⁻¹
Hydroxide, [OH ⁻] = 0.5 mM	Current Density = 11.2 A/m ²	95% Confidence Interval of k = 0.009 min ⁻¹
		Mass Transfer Based Reaction Coefficient, k _m = 0.00047 m/min
		95% Confidence Interval of k _m = 0.00015 m/min



Reaction Time (hr)	Reaction Run 1		Reaction Run 2		Reaction Run 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	8.322	n.a.	8.412	n.a.	7.744	n.a.
5	5.889	n.a.	7.226	n.a.	6.188	n.a.
10	4.782	n.a.	7.389	n.a.	4.406	n.a.
15	4.742	n.a.	7.233	n.a.	4.158	n.a.
20	3.558	n.a.	7.236	n.a.	3.166	n.a.
25	2.716	n.a.	5.584	n.a.	2.616	n.a.
30	2.216	0.0393	4.554	0.0501	2.207	0.0511
60	1.322	0.0306	2.856	0.0504	1.032	0.0297
90	1.176	n.a.	1.068	0.031	0.256	0.035
120	0.585	0.0232	0.374	0.0102	0.073	0.0172
180	0.354	n.a.	0.136	n.a.	0.036	n.a.
240	0.041	n.a.	n.a.	n.a.	0.057	n.a.

Table E- 8. Reaction kinetic data for the alkaline assisted electrochemical reduction of RDX, experiment #8.

Run: 8 Benchtop Pilot Reactor		1 st Order Reaction Coefficient, k = 0.057 min ⁻¹
Hydroxide, [OH ⁻] = 0.5 mM	Current Density = 22.4 A/m ²	95% Confidence Interval of k = 0.006 min ⁻¹
		Mass Transfer Based Reaction Coefficient, k _m = 0.00096 m/min 95% Confidence Interval of k _m = 0.00010 m/min

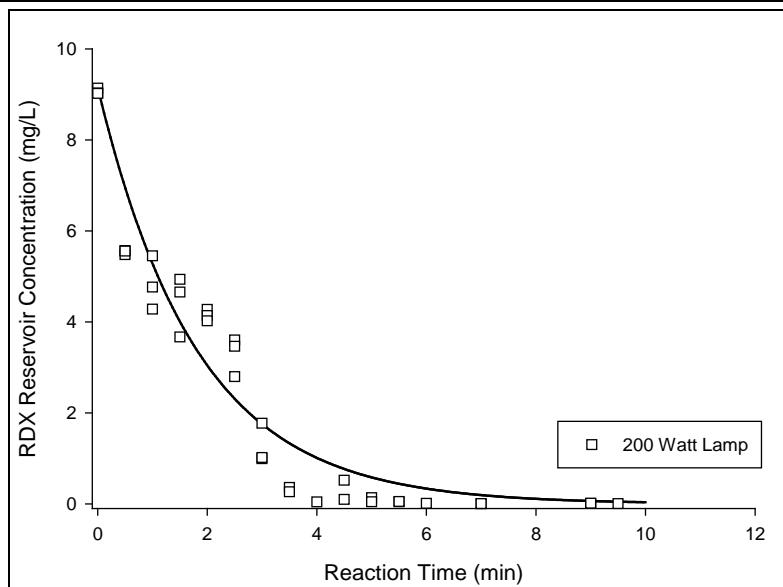


Reaction Time (hr)	Reaction Run 1		Reaction Run 2		Reaction Run 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0	8.016	0.3557	7.575	n.a.	8.254	n.a.
5	6.325	0.3086	5.738	n.a.	4.668	n.a.
10	4.327	n.a.	3.968	n.a.	5.218	n.a.
15	3.258	0.2079	2.868	n.a.	2.699	n.a.
20	2.297	0.1823	2.707	n.a.	2.672	n.a.
25	1.897	0.333	2.007	n.a.	2.217	n.a.
30	1.672	0.0512	1.614	0.011	1.203	0.0218
60	0.286	0.0428	0.36	0.0303	n.a.	0.1817
90	0.181	0.0247	0.057	n.a.	n.a.	0.019
120	0.122	0.0288	n.a.	n.a.	0.161	n.a.
180	0.089	0.0279	n.a.	n.a.	0.103	n.a.
240	0.045	0.0306	n.a.	n.a.	0.136	n.a.

Appendix F. Supporting Data for Ultraviolet Oxidation of RDX

Table F - 1. Reaction kinetic data for ultraviolet oxidation of RDX with a 200 W lamp

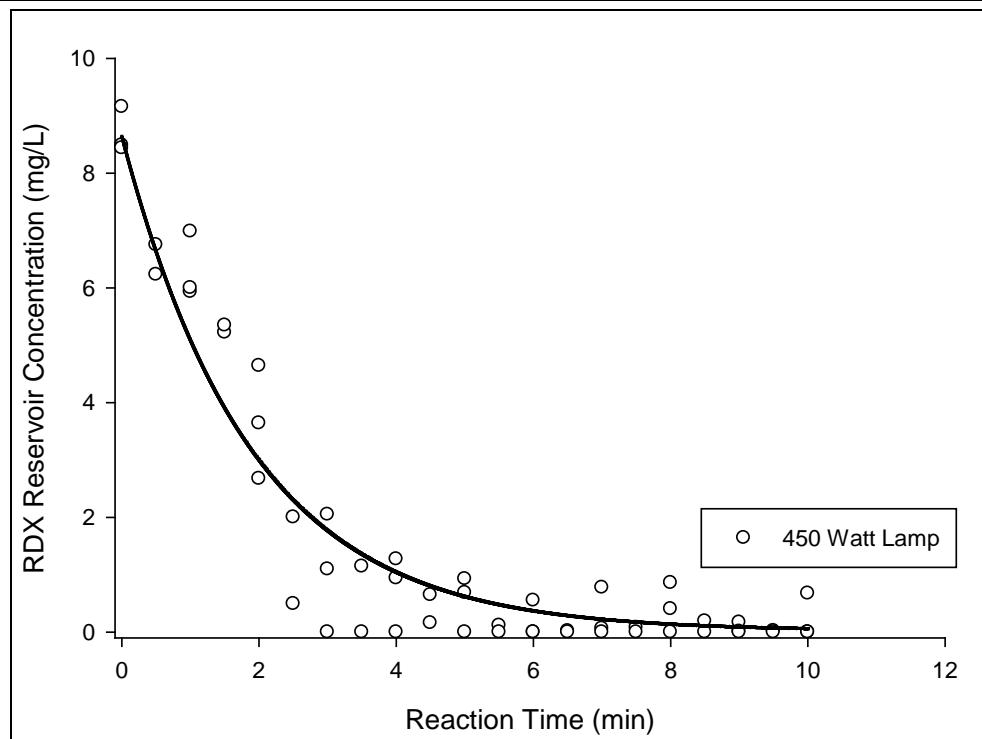
Experiment 1		Ultraviolet Oxidation	
Lamp Power =	200 W	1 st Order Reaction Coefficient, k =	0.90 min ⁻¹
Reactor Volume =	2 L	95% Confidence Interval of k =	0.02 min ⁻¹



Reaction Time (min)	Run 1		Run 2		Run 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0.0	9.138	n.a.	9.031	n.a.	9.022	n.a.
0.5	5.568	n.a.	5.479	n.a.	5.557	n.a.
1.0	5.454	n.a.	4.766	0.1019	4.282	0.2196
1.5	3.67	0.1486	4.936	0.148	4.656	n.a.
2.0	4.277	n.a.	4.142	0.1794	4.025	n.a.
2.5	2.8	0.2776	3.604	0.1481	3.465	0.0814
3.0	0.995	0.1498	1.774	n.a.	1.022	n.a.
3.5	0.362	0.0834	n.a.	n.a.	0.267	n.a.
4.0	0.046	0.018	n.a.	n.a.	n.a.	n.a.
4.5	0.101	0.0124	0.521	n.a.	n.a.	n.a.
5.0	0.139	0.0122	0.049	n.a.	n.a.	n.a.
5.5	0.049	n.a.	0.054	0.0119	n.a.	n.a.
6.0	0.015	n.a.	n.a.	n.a.	n.a.	n.a.
6.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
7.0	0.005	n.a.	0.009	n.a.	n.a.	n.a.
7.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
8.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Table F - 2. Reaction kinetic data for ultraviolet oxidation of RDX with a 450 W lamp

Experiment 2		Ultraviolet Oxidation		
Lamp Power =	450 W	1 st Order Reaction Coefficient, k =	0.84	min ⁻¹
Reactor Volume =	2 L	95% Confidence Interval of k =	0.02	min ⁻¹



Reaction Time (min)	Run 1		Run 2		Run 3	
	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)	RDX Conc (mg/L)	MNX Conc (mg/L)
0.0	8.487	n.a.	9.157	n.a.	8.434	n.a.
1.0	6.982	n.a.	6.231	0.1092	6.748	n.a.
2.0	4.642	n.a.	5.933	0.1019	6	0.1273
3.0	2.048	n.a.	5.219	0.1025	5.346	0.0917
4.0	1.271	n.a.	3.64	0.1982	2.676	n.a.
5.0	0.927	n.a.	2.002	n.a.	0.494	n.a.
6.0	0.552	n.a.	1.095	n.a.	n.a.	n.a.
7.0	0.776	n.a.	1.146	n.a.	n.a.	n.a.
8.0	0.859	n.a.	0.94	n.a.	n.a.	n.a.
9.0	0.171	n.a.	0.647	n.a.	0.159	n.a.
10.0	0.674	n.a.	0.686	n.a.	n.a.	n.a.

REPORT DOCUMENTATION PAGE

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14. ABSTRACT Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is the primary constituent in the explosive munitions that are produced at Holston Army Ammunition Plant (HSAP), Kingsport, TN. Part of a modernization effort for the 66-year-old plant includes the goal of zero RDX discharge to the facility industrial wastewater treatment plant. This study examines multiple technologies for removing RDX from the process waste stream at Holston Army Ammunition Plant. The treatment technologies evaluated included granular activated carbon (GAC), anoxic biotreatment, zero-valent iron (ZVI), alkaline hydrolysis, ultra-violet oxidation, and electrochemical decomposition. Evaluation criteria include capital and operating cost, and effectiveness in transforming RDX to nontoxic end products. Based on laboratory assessments using site water, alkaline hydrolysis and electrochemical treatment were selected for pilot scale evaluation. The RDX removal half-lives for the selected technologies were on the order of 0.25 hr with decomposition of RDX from 10,000 µg/L to less than 20 µg/L.					
15. SUBJECT TERMS Alkaline hydrolysis Anoxic biotreatment Electrochemical decomposition			Granular activated carbon (GAC) Holston Army Ammunition Plant RDX		Wastewater Ultra-violet oxidation Zero-valent iron
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